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On the Statistical Mechanics of Liquids, and the Gas of Hard Elastic Spheres

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Because of the extreme complications arising from a direct deductive approach, the theory of the liquid state requires the use of a model involving simplifying assumptions. In this paper an attempt is made to formulate general principles which any such model must follow. The first step is a general discussion of "communal" entropy, arising from the sharing of available space by all the atoms. Arguments are advanced to support the contention that for a gas of hard elastic spheres the communal entropy is fully excited in each direction of space, and amounts in all to $3R$ per mole. The communal entropy of assemblages of atoms exerting normal attractive and repulsive forces (in particular, the Debye solid) is considered. The geometry, the equation of state, and the partition function for an assemblage of hard elastic spheres are considered in detail. By extension of these ideas, allowing for the type of force actually exerted on each other by real atoms, a general form of partition function for a monatomic liquid is set up. This partition function involves a sum of two parts, one corresponding to a vibrational motion expressed in terms of the Debye characteristic temperature of the solid, and the other being a translational term, each part carrying with it its own communal entropy.

RECENT attempts to elucidate the properties of liquids and the melting phenomena may be divided into three classes. First there is the attempt to proceed deductively from the general principles of statistical mechanics to find the connection between the properties of individual atoms or molecules and their behavior en masse. This procedure is exemplified by the work of Kirkwood and Monroe[1] and that of Mayer.[2] Another method is to set up a model, i.e., make certain assumptions *a priori* regarding the partition function for the liquid, and use this to describe, rather than deduce, its properties. To this class belongs the work of Lennard-Jones and Devonshire, Alter, Walter and Eyring, Harasima, and others.[3] My own work[4] might be said to belong to this class, since in some cases models were used to get partition functions, but on the whole could perhaps be better described as inductive, as I have attempted to start with the known properties of the liquid, and from these infer the behavior of the molecules which give rise to these properties.

Each one of these procedures has its advantages, and the papers of various authors supplement each other in such a way that we are gradually acquiring an understanding of the liquid state. That each one of these procedures

[1] J. G. Kirkwood and E. Monroe, J. Chem. Phys. **9**, 514 (1941).
[2] J. E. Mayer, J. Chem. Phys. **10**, 629 (1942).
[3] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. **A163**, 53 (1937); **A165**, 1 (1938); **A169**, 317 (1939); **A170**, 464 (1939). W. Alter, J. Chem. Phys. **5**, 577 (1937). J. Walter and H. Eyring, J. Chem. Phys. **9**, 393 (1941). A. Harasima, Proc. Phys. Math. Soc. Japan **21**, 156 (1939).
[4] O. K. Rice, J. Chem. Phys. **6**, 472 (1938); **7**, 883 (1939); **9**, 121 (1941).

also has its disadvantages is obvious from the general agreement that, in spite of much progress, our understanding of the liquid state is still far from being satisfactory or complete. The direct deduction from statistical mechanics is theoretically the most desirable method of procedure, and would answer all questions regarding the liquid state, if it could be carried out. Unfortunately, it leads to such great mathematical difficulties that it becomes necessary to make many approximations along the way. On account of the mathematical complexity, it is difficult to evaluate the importance of these approximations, and it is equally difficult to evaluate the effects of special assumptions regarding such quantities as the parameters determining interatomic forces. In the end, one is practically reduced to the use of a model. On the other hand, in the theories which do use a model from the beginning, there is often some difficulty in seeing just how this model is related to the actual motions and properties of the individual molecules. Even though the models may reproduce experimental results over at least a limited range of conditions, there is an atmosphere of unreality about them. It appears to me that what is needed is a model which is as pictorial as possible, and is based, as closely as may be, upon the actual behavior of the atoms or molecules in a liquid. On the other hand, we also require some discussion to elucidate the general principles which may guide us in the choice of a model, and help us avoid concealed inconsistencies. The present paper represents an attempt at such a discussion. In a later publication the results will be applied to the experimental material available in the case of argon.

Before proceeding to details, we indicate in a general way the questions we believe need to be resolved, and the general method of attack. The first matter which needs to be cleared up is the contribution of the "communal entropy" to the total entropy of solids and liquids. The term "communal entropy" was introduced by Hirschfelder, Stevenson, and Eyring[5] to describe that contribution to the entropy due to the sharing of a volume by many molecules, and at the same time was believed by them to constitute the principal portion of the entropy of fusion in simple liquids. It was the cause of many impolite words at various symposia, but recently, since the abandonment of the idea that it had any direct connection with the entropy of fusion, there has been little discussion of it. It is true that the question could be side-stepped by a deductive approach from statistical mechanical principles, but any model we may introduce requires the discussion and evaluation of the communal entropy. The first portion of the paper will be devoted to a consideration of this matter.

With this preliminary question out of the way, we shall describe some experiments with glass spheres, made in the hope of elucidating some of the complicated geometrical problems connected with a random arrangement of monatomic molecules. We shall then discuss in some detail the statistical mechanics of a gas of hard elastic spheres, extending the work of Tonks,[6] and, finally, we shall proceed to a discussion of the general form for a partition function for the liquid state, basing it upon a generalization, to take care of intermolecular forces, of the results obtained for the gas of hard elastic spheres. Certain details may be left to be decided by experiment, and this will be done in later work.

Throughout we use the limiting high temperature form for all partition functions, as this is satisfactory for almost all liquids.

1. THE COMMUNAL ENTROPY OF A CONDENSED SYSTEM

In the paper in which they first used the term "communal entropy" Hirschfelder, Stevenson, and Eyring[5] gave it, in general, only a very vague definition, as that portion of the entropy which arises from the communal sharing of the volume available to the system by all the molecules. In order to make this definition precise, it is necessary to assign to each molecule a cell, representing its share of the total volume, and then calculate the entropy of the system assuming each molecule confined to its own cell; any excess of entropy of the actual system in which the molecules are not confined to their own cells is called the communal entropy. In the case of a gas of point molecules, or any sufficiently dilute gas, the manner of assigning the cells is very clear; the cell for each

[5] J. Hirschfelder, D. Stevenson, and H. Eyring, J. Chem. Phys. **5**, 896 (1937).

[6] L. Tonks, Phys. Rev. **50**, 955 (1936).

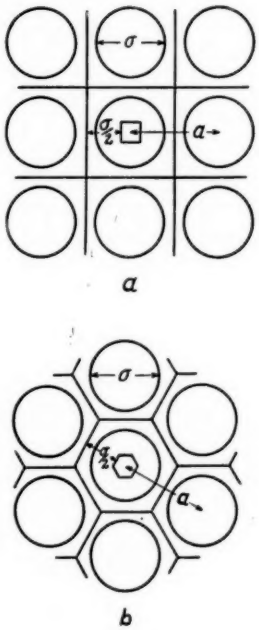

FIG. 1.

molecule is set equal to the total volume divided by the number of molecules. This is exactly what Hirschfelder, Stevenson, and Eyring did, thereby obtaining a very definite value of R per mole for the communal entropy. The danger lies in applying this result to other cases. In every case it is necessary to consider specifically the assignment of the cells to each molecule. In some cases it may not be possible to make any reasonable assignment; then the communal entropy cannot be defined. It does seem to be possible, however, to make the assignment in the case of closely packed hard elastic spheres, and it is of importance in determining the partition function.

The simple case of a one-dimensional system of N hard spherical atoms (or molecules—we use the words interchangeably) of diameter σ, whose centers are constrained to move along a straight line of length l, was considered by Tonks.[6] For this system he calculated the phase integral explicitly; his value can be put in the form $l^N(1-\theta_1)^N/N!$ where $\theta_1=N\sigma/l$. If this result is multiplied by the momentum integral and divided by h, and if $N!$ is evaluated by Stirling's theorem, we get for the partition function referred to a single atom (omitting factors which will be negligible, on account of the large value of N, when the logarithm is taken),

$$Q=(2\pi mkT/h^2)^{\frac{1}{2}}e(l/N)(1-\theta_1). \qquad (1)$$

If we assign a cell of length l/N to each sphere, and assume the sphere constrained to stay inside its own cell [thus giving it a free distance of $(l/N)(1-\theta_1)$], the partition function will be

$$Q=(2\pi mkT/h^2)^{\frac{1}{2}}(l/N)(1-\theta_1). \qquad (1')$$

The factor e in Eq. (1) arises because the length l is shared by all the atoms, and we see that this assignment of cells gives a communal entropy which, per mole, is equal to $R\ln e=R$, and, in this case, is independent of the closeness of the packing.

The assignment of cells in a two- or three-dimensional gas of hard elastic spheres is scarcely more difficult if the packing is simple cubic, and if the spheres are sufficiently closely packed. When the packing is very close, the motion of the atoms in any direction will always be so small as not to interfere appreciably with motions at right angles; in this case the motion may be considered as compounded of independent one-dimensional motions along the mutually perpendicular, interpenetrating rows of atoms. The type of cell to be assigned is indicated in Fig. 1a for the two-dimensional case. The little square shows the possible region of motion of the center of the atom, which is the important thing. In three dimensions it is a little cube, whose edge will be $a-\sigma=v^{\frac{1}{3}}-\sigma=v^{\frac{1}{3}}(1-\theta^{\frac{1}{3}})$ where v is the volume per atom, a is the mean interatomic distance, and $\theta=\sigma^3/v$. In view of the independence of the motions in the three directions of space, the partition function will be just the cube of that in Eq. (1) with $v^{\frac{1}{3}}(1-\theta^{\frac{1}{3}})$ substituted for $(l/N)(1-\theta_1)$. Thus

$$Q=[(2\pi mkT/h^2)^{\frac{1}{2}}ev^{\frac{1}{3}}(1-\theta^{\frac{1}{3}})]^3. \qquad (2)$$

This means that the communal entropy per mole is equal to $3R\ln e=3R$, one k per atom for each degree of freedom, since if the atoms were confined to their own cells the e would not appear inside the bracket. I have recently called attention to the large value of the communal entropy,[7] but, though it was clearly implied in Tonks' work,[6] this was apparently not realized by Hirschfelder, Stevenson, and Eyring in their first

[7] O. K. Rice, J. Chem. Phys. **10**, 653 (1942).

paper on the subject, nor by others (including myself) in the subsequent discussion.[8]

We must now consider the case of a close-packed instead of a simple cubic arrangement. (We here use the term "close-packed" in the technical sense of describing hexagonal or, usually, in three dimensions, cubic close-packing, as contrasted to the term "closely packed" which merely indicates that the atoms are close together.) In the two-dimensional case the appropriate cell assignment, which avoids any overlapping of spheres, is a hexagon, as shown in Fig. 1b (compare Tonks' Fig. 4). The area of the small hexagon which gives the free area of motion of the center of the atom is obviously $s[(a-\sigma)/a]^2$ where s is the atomic area. In three dimensions the cell is a dodecahedron, the free volume per atom being a small dodecahedron of volume $v[(a-\sigma)/a]^3=v(1-\theta^{\frac{1}{2}})^3$, where v is as before the atomic volume and θ is given in this case by

$$\theta=\sigma^3/a^3=\sigma^3/2^{\frac{1}{2}}v, \tag{3}$$

since v is equal to $a^3/2^{\frac{1}{2}}$. (We shall hereafter, unless otherwise noted, consider θ to be defined by Eq. (3) in the three-dimensional case. For the one-dimensional case, we shall continue to use the subscripted θ_1.) We now ask whether or not the communal entropy is excited as before, i.e., whether or not we can use Eq. (2) unchanged except that θ is given by Eq. (3).

We may note that there are two distinct questions involved here. In the one-dimensional case, in which the communal entropy is fully excited, free fluctuations of the position of atoms (without change in their ordinal position), are allowed all along the line on which they move. Such fluctuations, which may become very large, are blocked to some extent by the neighboring rows in the close-packed lattice, even if the atoms in the designated row do not move laterally out of the row at all. On the other hand, if an atom does move laterally out of its row, its free motion parallel to this row cannot be so great as it was before, even if all the neighboring atoms remain fixed in their average positions. This latter effect is presumably taken care of, at least approximately, by using the value of v calculated for the cubic close-packed lattice and by using Eq. (3) in the determination of θ (equivalent to using the dodecahedral cell). To find out about the excitation of communal entropy, we must consider the fluctuation along a row of atoms, assuming the centers to be constrained to stay on a straight line. If the fluctuations are not too greatly interfered with by interlocking atoms, we may again consider the excitation of communal entropy to be complete in the three dimensions of space, and though the geometry of the system is somewhat different than in the simple cubic case, it would appear that we could not be greatly in error in assuming that the dodecahedron giving the free volume is effectively expanded by a factor of e in all its linear dimensions, again giving a communal entropy of $3R$.

Suppose, then, we have a row of N hard elastic spheres arranged in a straight line, which can move freely along the line except that they cannot penetrate into or pass each other. With a length of line l, of which the portion l_1 is to the left of the edge of the atom whose fluctuations are being considered, when it is in its average position, and the portion l_2 to the other side (so that $l_1+l_2=l-\sigma$), and with the diameters of the $N-1$ other atoms occupying a fraction θ_1 of the length l_1+l_2, a simple calculation of the standard type (see the Appendix) gives as the approximate probability of a fluctuation in position of amount Δl

$$P=P_0\exp\left[-(N-1)(\Delta l)^2/2(1-\theta_1)^2l_1l_2\right]. \tag{4}$$

The exponent is equal to -1 when the value of Δl is equal to

$$\lambda=[(1-\theta_1)/(N-1)][2l_1l_2(N-1)]^{\frac{1}{2}}. \tag{5a}$$

For the middle atom, for which $l_1=l_2=(l-\sigma)/2$

$$\lambda=[(l-\sigma)(1-\theta_1)/(N-1)][(N-1)/2]^{\frac{1}{2}}, \tag{5b}$$

$(l-\sigma)(1-\theta_1)/N$ is the free length per atom.[9] About 80 percent of the fluctuations are less than

[8] Since the communal entropy of a dilute gas is only R per mole, one is led to suppose that the decrease from $3R$ for hard elastic spheres at high concentration must occur at some intermediate stage. Presumably this will happen when displacements can become so great that holes of atomic size begin to be probable, and there is much lateral distortion of rows and columns. But in this situation it becomes difficult to assign a cell to each molecule, and it is not possible to set up an unambiguous definition of communal entropy, so that a detailed discussion of the change in its value is useless—fortunately, for the theory of liquids ideas based on a fairly closely packed set of spheres seem to be adequate.

[9] See the end of the Appendix.

TABLE I.

N	Fluct. ratio	Entropy discrep.
5	2.0	0.33
13	2.8	.19
21	3.5	.14
29	4.0	.11

λ. From Eq. (5a) or (5b), however, it appears that λ can increase indefinitely as N increases. Enormous fluctuations, therefore, become appreciably probable.

With a cubic or hexagonal close-packed arrangement the interlocking effect of the adjacent atoms must necessarily be to prevent these enormous fluctuations. The question which must be answered is, therefore, how important are large fluctuations for the full excitation of communal entropy. That they will not be so extremely important is clear from the discussion of Gurney and Mott,[10] who pointed out that for a finite collection of N atoms along a line the communal entropy is $R\ln(N/N!^{1/N})$ instead of R, and that this approaches R, as N increases, fairly rapidly. However, we need to consider for different values of N, actual values of the expression $R\ln(N/N!^{1/N})-R$, which we shall call the "entropy discrepancy," and, simultaneously, the actual probable fluctuation, which can best be measured as the "fluctuation ratio," $\lambda : (l-\sigma)(1-\theta_1)/N=[(N-1)/2]^{\frac{1}{2}}N/(N-1)$. The fluctuation ratio is the ratio between the probable fluctuation λ and the free length per atom; since this depends on N we wish to see whether, by assuming the atoms blocked off in groups of N, it can be made sufficiently small while the entropy discrepancy is still small.

Before we do this, however, let us make an observation which will strengthen our argument. Consider the free space available for the motion of even an individual atom. Tonks has shown that the average distance between two next-nearest neighbors (i.e., between a pair of atoms with another atom between them) is just equal to what it would be if all atoms were uniformly spaced on the line, namely, $2l/N$. If, therefore, we fixed, in an average position, all the atoms but one, it would move through a distance $2(l/N)(1-\theta_1)$ rather than merely $(l/N)(1-\theta_1)$, as would be the case if the atoms were all partitioned into equal lengths on the line. Thus if we considered only the motion of the individual atoms, assuming each to be free to move in the average "field" of its neighbors, we already have a factor 2 (instead of e) in the partition function, and so may be said in this approximation to have accounted for about 69 percent [i.e., $(R\ln 2)/R$] of the communal entropy.

Extending this same idea to a row of N atoms in a length l, or free length $l(1-\theta_1)$, we see that, if these N atoms are simply imbedded in a longer row of atoms, we should add one atomic free length $(l/N)(1-\theta_1)$ to the free length $l(1-\theta_1)$. This changes Gurney and Mott's formula for the communal entropy of the row to $R\ln[(N+1)/N!^{1/N}]$ and also multiplies the fluctuation ratio by a factor $(N+1)/N$.

Allowing for these corrections, we show in Table I the entropy discrepancy and the fluctuation ratio for a number of different values of N. For a three-dimensional case, of course, the entropy discrepancy must be multiplied by three to get the total for all three degrees of freedom, but even allowing for this, it appears that the entropy discrepancy has become quite small, say at $N=21$, before the fluctuation ratio has become large enough to indicate that the fluctuation will be appreciably affected by the interlocking action of the atoms in adjacent rows. Of course there will be some blocking of the free motion of a group of, say, 21 atoms, but on the other hand, fluctuations involving any such given group and an adjacent group simultaneously will be by no means entirely cut out, since the selection of the particular atom which starts the group is quite arbitrary. Thus it appears altogether probable that the assumption of complete excitation of communal entropy is a reasonably good approximation, not in error by more than a few tenths of an entropy unit at most, even in three dimensions.

This conclusion is strengthened by looking at the matter in another way. Consider a group of atoms in close-packed array, as indicated in Fig. 2a. If in pursuance of its fluctuations, in order to make the most of its possibilities of communal entropy, the atom A moves to the position near atom B, shown in Fig. 2b, it is true that it

[10] R. W. Gurney and N. F. Mott, J. Chem. Phys. **6**, 222 (1938).

blocks the motion of D to some extent. On the other hand, greater free space is left for atom E. Also the possibility of fluctuations of atom A perpendicular to the row BC is not prevented if it takes the position indicated in Fig. 2b. Of course, if it moves out of the row its freedom of motion in the direction parallel to that row is somewhat less, but, as already noted, this is taken account of in the definitions of v and of θ in the three-dimensional close-packed lattice.

Let us now consider the situation which exists when the atoms are not simply hard elastic spheres, but exert forces on each other. In this case it is not easy to define a cell for each atom in an unambiguous way. Yet I believe that we may define the communal entropy in an operational manner which is sufficiently analogous to the way it is defined for hard spheres. The matter is of interest, for in the theory of the liquid state we shall wish to combine partition functions of different types, and we should hesitate to do this if the excitation of communal entropy were too radically different in the different partition functions.

We consider first the one-dimensional case. If the two end atoms are held fixed in position, the other atoms will have equilibrium positions equally spaced along the line. If the vibrations are small enough so that the oscillations of the system may be assumed to be harmonic, and if an atom is acted upon only by its nearest neighbors, the partition function can be worked out completely.[11] Let ξ_i be the displacement of the ith atom from its equilibrium position, and let ξ_{i-1} and ξ_{i+1} be the displacements of its two neighbors. The force acting on ith atom due to these displacements may be written $b(\xi_{i-1}+\xi_{i+1}-2\xi_i)$, where b is the force constant. If now the $(i-1)$th and $(i+1)$th atoms are held fixed at their equilibrium positions, the ith atom can vibrate about its equilibrium position with a frequency given by

$$\bar{\nu}=\pi^{-1}(b/2m)^{\frac{1}{2}}. \tag{6}$$

If, however, all the atoms are free to vibrate, except the two end ones which are fixed in position, they execute certain normal vibrations, and if there are $N+2$ atoms (including the fixed end ones) there will be N such vibrations, whose frequencies can be found by giving n all integral values from 1 to N in the following expression (which assumes N very large)

$$\nu=\pi^{-1}(b/m)^{\frac{1}{2}}\sin\left[(\pi/2)(n/N)\right]. \tag{7}$$

It will be noted that the average of the square of these "perturbed" frequencies is equal, as it must be, to $\bar{\nu}^2$.

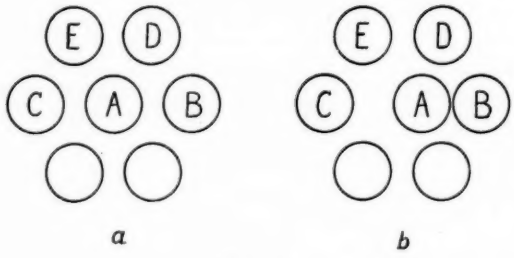

FIG. 2.

The partition function for a single atom, vibrating in the field of its fixed neighbors, is equal to $kT/h\bar{\nu}$. The motion of the single atom with fixed neighbors is analogous to the motion of a single atom through the free space equal to $2(l/N)(1-\theta_1)$ (i.e., the free space from neighbor to neighbor, or *twice* the single atom's quota of free space) in the case of hard elastic spheres. We might expect, therefore, that the partition function for the whole assembly of atoms would be obtained by multiplying $kT/h\bar{\nu}$ by the factor $e/2=1.359$ (i.e., multiplying $kT/2h\bar{\nu}$ by the factor e) in order to take care of the communal entropy. To find the actual value of the partition function we must find the average value of $\ln(kT/h\nu)$ for all the frequencies given by Eq. (7) and take the exponential of the result. The average of $\ln(kT/h\nu)$ is $N^{-1}\int_0^N \ln(kT/h\nu)dn$. Using Eq. (7), evaluating this integral, and taking its exponential, we find for the partition function $2^{\frac{1}{2}}kT/h\bar{\nu}=1.414kT/h\bar{\nu}$. We might, therefore, say that in this case the communal entropy is about $\ln(2\times1.414)/\ln e=104$ percent excited.

In the three-dimensional case the problem of finding an exact expression, such as Eq. (7), for the frequencies is much more complicated.[12] However, we may use the Debye distribution of frequencies with a reasonable degree of approximation, and in this case it is known that the partition

[11] See J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, New York, 1940), pp. 246–248.

[12] An exact value for the partition function has been obtained in some special cases. See M. Born and M. Bradburn, Proc. Camb. Phil. Soc. **39**, 100, 104, 113 (1943).

function per molecule is $e^{\frac{1}{2}}kT/h\nu_m$ where ν_m is the Debye maximum frequency. Also it is known that $\nu_m=(5/3)^{\frac{1}{2}}\bar{\nu}$, where $\bar{\nu}$ is the frequency of a single atom vibrating in the field of its fixed neighbors,[13] so the partition function becomes $(3/5)^{\frac{1}{2}}e^{\frac{1}{2}}kT/h\bar{\nu}=1.082kT/h\bar{\nu}$. In this case, therefore, the communal entropy is only about $\ln(2\times1.082)/\ln e=77$ percent excited, due to the geometrical factors which determine the frequency distribution. It may be noted that $\bar{\nu}$ will also be larger than it would be in a one-dimensional line of atoms having the same law of force, on account of the effects of the atoms to the side of the line of vibration.[14] This, however, cannot be properly said to have anything to do with the communal entropy, but may have considerable to do with the fusion process, for, as we shall see, this constraining effect of the side atoms is probably largely, if not completely, relaxed in the liquid state.

2. THE GEOMETRY OF A DISORDERED ASSEMBLY OF SPHERES

Since we wish to pursue as far as possible the analogy between a real liquid and a gas of hard elastic spheres, it will be desirable to have as much information about the geometry of the latter as possible. If we suppose that at very small volumes the spheres are arranged in a face-centered cubic packing, we realize that as we allow the volume to increase, this regular arrangement of the spheres will at some time break down in favor of a random arrangement. The question arises, what will be the smallest possible volume at which a completely random arrangement can occur. This is a question which does not appear to be answerable by conventional geometrical methods, but it may readily be answered by experiment. As a matter of fact, experiments of this nature have been performed, though with a different object in view, by Westman and Hugill.[15]

Our experiments consisted of pouring water into a known volume filled with glass beads of the type used in filling fractionation columns. In this way the fraction of the volume actually used by the glass beads could be determined. Since a similar fraction for cubic close-packing can be calculated, it becomes a simple matter to determine the increase of volume on going from cubic close-packing to random close-packing.

The beads used were examined, and obvious off-size and defective ones discarded, to get an assemblage of beads which were reasonably spherical and fairly uniform in size. In making the measurements it was also necessary to consider the edge effect, due to the extra amount of empty space at the surface of the vessel. In order to estimate this effect, various sized beads and vessels were used, ranging from about 400 cc of beads of 0.44-cm diameter in an 800-cc beaker, to about the same volume of beads of 1.6-cm diameter in a 600-cc beaker. The extra volume at the surface was found to be equal to $\sim0.13\times$radius of bead$\times$area of surface. This is very reasonable, since it can be seen that the spheres at the edge tend for the most part to touch the surface, and have the appearance of being close-packed over considerable areas. It can be shown that, if a cubic close-packed arrangement is split between its densest planes, an extra volume is included between it and a plane surface equal to $0.11\times$radius$\times$area of surface.

As a result of these experiments, I conclude that the volume of a random arrangement of an indefinite assemblage of spheres exceeds that of the cubic close-packed arrangement by 15 (±3) percent. Westman and Hugill obtained about 20 percent increase.

3. THE EQUATION OF STATE OF A GAS OF HARD ELASTIC SPHERES

As already noted, the equation of state of a gas of hard elastic spheres has been considered in some detail by Tonks.[6] For a very dilute gas Tonks used the equation due to Boltzmann,[16] which gives the pressure-volume product correct to the third virial coefficient, namely,

$$pV/RT=1+(b/v)+\tfrac{5}{8}(b/v)^2. \qquad (8)$$

Here V is the molal volume, while v is the volume per molecule, and b is van der Waals' excluded volume. $b=\frac{2}{3}\pi\sigma^3$, where σ is the molecular diame-

[13] See O. K. Rice, J. Am. Chem. Soc. **63**, 3 (1941).
[14] See reference 13, p. 4.
[15] A. E. R. Westman and H. R. Hugill, J. Am. Ceramic Soc. **13**, 767 (1930).
[16] L. Boltzmann, *Vorlesungen über Gastheorie*, Part II, §§ 48–52. Equation (8) has been extended to the fourth virial coefficient by Boltzmann, K. Acad. Wet. Amst., Proc. Sec. Sci. **1**, 398 (1899); H. Happel, Ann. d. Physik **21**, 342 (1906); and R. Majumdar, Bull. Calcutta Math. Soc. **21**, 107 (1929).

ter. Equation (8) has also been deduced by Ursell,[17] by a more general method, which theoretically could be extended to give the complete series. However, this involves some exceedingly difficult calculations, and has not actually been carried out. Tonks' procedure was to use Eq. (8) for large volumes, and the pressure derived from Eq. (2) for small volumes. For intermediate volumes he simply interpolated. However, using the thermodynamic relationship $(\partial S/\partial V)_T=(\partial p/\partial T)_V$, I showed[18] that his interpolation implied a close-packed gas with communal entropy more nearly equal to $3.5R$ than to $3R$. I, therefore, suggested a different interpolation, which appeared just as reasonable and made the communal entropy come out about right. The interpolation does, however, cover a rather wide gap. It, therefore, seems desirable to try to bridge this gap, at least in part. Even though the gas of hard elastic spheres is a purely artificial problem, the geometrical features involved are sufficiently near to those of real liquids, to make any progress in this direction valuable.

We proceed by using the virial of Clausius,[19]

$$pV=\tfrac{1}{3}\Sigma mu^2+\tfrac{1}{3}\Sigma\Sigma r\phi(r),$$

where u is the molecular velocity and m the molecular mass, the sum being taken over all molecules, and where r is the distance between a pair and $\phi(r)$ the force of repulsion between them, the double sum being taken over all pairs. For one mole $\frac{1}{3}\Sigma mu^2=RT$. In the case of hard elastic spheres there is no force between a pair unless they are in collision. While they are in collision an average force $\bar{\phi}$ is exerted such that, if τ is the duration of the collision, $\bar{\phi}\tau=2\mu u_r$, where u_r is the relative velocity along the line of centers and μ is the reduced mass of the colliding pair ($\mu=m/2$). The factor 2 occurs because the relative momentum simply changes sign during a collision; therefore, the change in momentum is twice the momentum itself. If $\eta(u_r)du_r$ is the number of collisions occurring per second with relative velocities between u_r and u_r+du_r, the virial expression becomes

$$pV=RT+\tfrac{1}{3}\int_0^\infty 2\mu u_r\sigma\eta(u_r)du_r. \qquad (9)$$

In this expression the distance r at which the force acts is always equal to, and has been replaced by, σ. We now have to evaluate $\eta(u_r)$. For the first steps of this calculation we follow Boltzmann. Let us first consider a single pair of spherical molecules, and ask for the probability that their surfaces shall be within some very small distance δ of each other. If the gas is dilute we can give one of the molecules any position whatsoever in the volume V. The chance that the other one will lie within a distance δ is obviously very closely equal to the ratio of the volume of a shell of radius σ and thickness δ to the whole volume, i.e., $4\pi\sigma^2\delta/V$. Since each pair is independent of every other in this approximation, and since there are $N(N-1)/2\sim N^2/2$ pairs in a gas of N spheres, we get $2\pi\sigma^2\delta N^2/V$ for the total number of pairs which are within a distance δ. After a time δ/u_r all those moving toward each other with a relative velocity u_r will have collided. The number of collisions of such molecules per second will be, therefore, $\eta(u_r)du_r=\pi\sigma^2u_rN^2f(u_r)du_r/V$ where $f(u_r)du_r$ is the fraction having relative velocities in the indicated limits and account has been taken of the fact that half of the pairs are moving away from each other. Equation (9) then becomes

$$pV=RT+\tfrac{2}{3}(\pi\sigma^3N^2/V)\int_0^\infty \mu u_r^2 f(u_r)du_r$$
$$=RT[1+(b/v)], \qquad (10)$$

where v is the volume per molecule, since the integral is twice the average relative kinetic energy along the line of centers, and hence is equal to kT. Thus we derive the first two terms of Eq. (8). We now depart somewhat from Boltzmann's methods. We must take into account the effect of all the other molecules on the probability of the collision of any pair. To do this we need to know how the phase integral for all the other molecules changes when a given pair is in collision. Let us now place the whole system in a cylinder with a weighted piston which exerts on the system the external pressure p, necessary to maintain equilibrium. In order to find the phase

[17] See R. H. Fowler, *Statistical Mechanics* (The Macmillan Company, 1936), second edition, pp. 245 ff.

[18] O. K. Rice, J. Chem. Phys. **10**, 653 (1942). *Erratum:* the ordinate in the figure in this note should have been labeled $R^{-1}v(\partial p/\partial T)_v$.

[19] See reference 17, pp. 286 ff, or Boltzmann, reference 16, §§ 49, 50.

integral of all other molecules we can assume that we manipulate the two colliding molecules at will. If these two are far apart they occupy a certain volume and carry with them exclusion spheres into which the other molecules cannot penetrate. If they are close together these exclusion spheres overlap. Therefore, in order to keep the phase integral of the rest of the spheres constant, the volume of the whole gas must be decreased by some amount ΔV (the *contraction* is taken as positive), depending upon the amount of overlapping of the exclusion spheres. Let the gas now expand to the original volume, keeping the spheres in contact. The change in the work function is $-p\Delta V$ (the pressure, of course, in all these processes being practically unchanged) and the phase integral is accordingly multiplied by a factor $\exp(p\Delta V/kT)$. This means that the probability of collision must be multiplied by this factor.[20] Equation (10) thus becomes

$$pV=RT[1+(b/v)\exp(p\Delta V/kT)]. \quad (11)$$

If the gas is dilute we may safely assume ΔV to be the overlapped volume of the exclusion spheres, which turns out to be[16] $\frac{5}{12}\pi\sigma^3$ or $\frac{5}{8}b$, hence

$$pV=RT\{1+(b/v)\exp[\tfrac{5}{8}(b/v)(pV/RT)]\}. \quad (12)$$

If the exponential is expanded and the solution for pV/RT started, it is readily seen that this coincides with Eq. (8), as far as the latter goes. If we write $pV/RT=y$ and $b/v=x$, Eq. (12) becomes

$$y=1+x\exp(\tfrac{5}{8}xy). \quad (13)$$

(From the definition of θ (Eq. 3) and b, we find $x=2.964\theta$.) We can solve for y as a function of x, which is proportional to the concentration. However, as x and y increase, it is found that the second term of the right-hand side of Eq. (13) shortly begins to increase very much more rapidly than y itself, and we soon reach a point (at about $x=0.63$ or $\theta=0.21$) where there are no further solutions of Eq. (13). Since for a close-packed system $\theta=1$ and for the randomly packed spheres θ is about 0.87, it is clear that this behavior does not correspond to reality and can only mean that at great densities the value of ΔV cannot be as great as the overlapped volume of the exclusion spheres of two spherical molecules.

[20] This method of treatment amounts to use of the local free energy. See J. G. Kirkwood, J. Chem. Phys. **7**, 919 (1939).

A little consideration shows that this must, indeed, be the case. For, as we withdraw the two manipulated spheres from each other, in the dense gas they begin to overlap the exclusion spheres of other molecules before their own cease to overlap. We may expect no further decrease in effective volume available to the rest of the molecules after the two manipulated spheres have been withdrawn to something like the average intermolecular distance in the gas. In particular, when the effective free volume has become zero and the pressure infinite Eq. (11) demands that $\Delta V=0$. In general we may write in place of Eq. (13)

$$y=1+x\exp(\tfrac{5}{8}fxy), \quad (14)$$

where f is a fraction to be determined, equal to the true effective value of ΔV divided by its "ideal" value $\frac{5}{12}\pi\sigma^3$.

To make an estimate of f we need to consider the situation more closely. Let us first consider the case in which the gas is still fairly dilute. If the two manipulated spheres are far apart, they exclude a certain volume of space equal to the sum of their exclusion spheres. However, the actual amount of space excluded is slightly reduced because these exclusion spheres occasionally overlap those of other molecules. This overlapping is in addition to that of the exclusion spheres of these other molecules among each other, and does not replace any of it if the gas is sufficiently dilute so that triple collisions are rare.

Let us calculate the average overlap of the exclusion sphere of a given molecule with those of other molecules. In a total volume V, occupied by N molecules, the probability that one of the $N-1\sim N$ other molecules be at a distance between r and $r+dr$ of the given one is $4\pi r^2Ndr/V=4\pi r^2dr/v$. If $r<2\sigma$, the overlapped volume may readily be shown to be[21] $\frac{4}{3}\pi\sigma^3-\pi\sigma^2r+\pi r^3/12$. Therefore the average overlap is

$$(4\pi/v)\int_\sigma^{2\sigma}\left(\frac{4}{3}\pi\sigma^3-\pi\sigma^2r+\frac{1}{12}\pi r^3\right)r^2dr. \quad (15)$$

This is the average overlap for *each* one of the manipulated spheres.

When the two manipulated molecules are in contact there is still a certain average overlap

[21] See reference 17, p. 250, or Boltzmann, reference 16, § 59.

with the exclusion spheres of other molecules. However, this overlap will be less than if the manipulated molecules are separated, for a certain portion, $\frac{5}{16}$, of their exclusion spheres is already overlapped. Any other molecule is prevented from entering certain regions near one of the manipulated molecules, and furthermore, overlapping of an already overlapped exclusion sphere is not fully effective in increasing the available volume. As a rough approximation we shall assume that when the two manipulated molecules are in contact with each other, the average overlap is $\frac{11}{16}$ of the expression given by Eq. (15). Contact of the manipulated molecules, therefore, results in a decrease of overlap with others of $\frac{5}{16}$ times the expression (15). $2\times\frac{5}{16}$ times the expression should be subtracted from the "ideal" value of ΔV, or $\frac{5}{12}\pi\sigma^3$, in order to get the effective ΔV or $f\Delta V_{\text{ideal}}$. The factor 2 arises because the overlapping with other molecules of both of the manipulated molecules is affected. The value of f is readily found to be

$$f=1-(48/5mv\sigma^3)\times\int_\sigma^{2\sigma}\left(\frac{4}{3}\pi\sigma^3-\pi\sigma^2 r+\frac{1}{12}\pi r^3\right)r^2dr, \quad (16)$$

where $m=16/(2\times5)=1.6$. This value of m, which holds only for the very dilute gas, is admittedly an approximation even for this case on account of the rough estimate of the amount of extra overlapping when the two manipulated atoms are in contact; actually, however, the results are very insensitive to it, and an error in this value of m of twofold would not be very serious, as was found by actual trial.

This treatment breaks down, of course, when the space becomes crowded with molecules. To find the average overlap in a dense gas, we shall consider a central molecule surrounded by m nearest neighbors, and we shall suppose that these m molecules have at their disposal a space equal to m molecular volumes. That is to say, we shall suppose them to be occupying a shell of inner radius σ and outer radius r_1 given by

$$\tfrac{4}{3}\pi(r_1^3-\sigma^3)=mv. \quad (17)$$

Provided the interference of the surrounding molecules with each other were independent of r, the probability of a nearest neighbor being between r and $r+dr(r<r_1)$ would be

$$4\pi r^2dr/\tfrac{4}{3}\pi(r_1^3-\sigma^3)=3r^2dr/(r_1^3-\sigma^3). \quad (18)$$

(If a molecule went beyond the distance r_1, it would cease to be a nearest neighbor, and another would in general take its place.) From this equation one could roughly calculate the average overlap of a pair of nearest neighbors. It is this average overlap of nearest neighbors which should be subtracted from ΔV_{ideal} in the case of a dense gas. For if we consider the two manipulated molecules we see that, if they are in what may be called an average position as nearest neighbors, we may exchange one of them with another "average" molecule elsewhere, and in a dense gas the amount of space available to the *other* molecules will still not be appreciably changed. In the dilute gas the overlapping of the exclusion spheres of other molecules with those of the manipulated molecules takes place independently of the overlapping of the exclusion spheres of these other molecules among themselves. But in the dense gas any motion of a molecule essentially becomes an exchange of position with another. If one of the manipulated molecules is moved from its average position as a nearest neighbor of the other manipulated molecule to a distant position, there is more overlapping of the exclusion spheres of the manipulated molecules with those of other molecules, but less overlapping, not only of the exclusion spheres of the manipulated molecules with each other, but also of those of the other molecules with each other. In a dense gas the possible average amount of overlapping is about fixed.

However, Eq. (18) needs some modification. It is obvious, of course, that according to it the average overlapping will always be less than ΔV_{ideal}, therefore, f must always be greater than zero. However, when the system approaches the state in which the molecules are random close-packed, corresponding to the assemblages described in Section 2 above, y must approach infinity. This being the case, we see by Eq. (14) that f must approach zero, otherwise the orders of infinity on the two sides of Eq. (14) would be different. We must suppose, therefore, that the average overlap approaches ΔV_{ideal}, which must mean that the average available free volume for any molecule must approach zero. The reason

that this happens is that the neighbors just outside the m nearest neighbors occupy some of the space inside the sphere of radius r_1. In fact, in the random close-packed arrangement they reduce it to zero.[22] As a better approximation we shall use instead of Eq. (17)

$$\tfrac{4}{3}\pi(r_1^3-\sigma^3)=mv-c, \tag{19}$$

where c is a constant to be evaluated by setting it equal to mv, when v is equal to the molecular volume of the random close-packed state and m the number of nearest neighbors in that state. As an approximation we may set under these conditions

$$v=(\sigma^3/2^{\frac{1}{2}})(12/m), \tag{20}$$

where $\sigma^3/2^{\frac{1}{2}}$ is the volume of the cubic close-packed arrangement with spheres in contact. This assumes that the volume per molecule varies inversely proportionally to the number of nearest neighbors. This is what actually would happen if the average number of nearest neighbors in a cubic close-packed system were reduced by removing molecules, leaving holes.[23] In any event, the matter is not very critical. From Eqs. (20) and (19), then

$$c=12\sigma^3/2^{\frac{1}{2}} \tag{21}$$

and from Eqs. (21) and (19)

$$r_1^3=(3/4\pi)mv-(9/2^{\frac{1}{2}}\pi-1)\sigma^3. \tag{22}$$

If we introduce a quantity ζ such that $\zeta=1$ if $r_1<2\sigma$ and $\zeta=2\sigma/r_1$ if $r_1>2\sigma$, we can, by making use of Eq. (18) and the expression for the overlapped volume just before Eq. (15), write the average amount of overlap in the general form

$$\frac{3}{r_1^3-\sigma_1^3}\int_\sigma^{r_1\zeta}\left(\frac{4\pi\sigma^3}{3}-\pi\sigma^2 r+\frac{\pi r^3}{12}\right)r^2dr$$

$$=\frac{\pi r_1^3\zeta^3}{r_1^3-\sigma_1^3}\left[\frac{4}{3}-\sigma^3-\frac{3}{4}\sigma^2 r_1\zeta\right.$$

$$\left.+\frac{1}{24}r_1^3\zeta^3-\frac{5}{8}\sigma^6 r_1^{-3}\zeta^{-3}\right]. \tag{23}$$

For f we get, by dividing by $\frac{5}{12}\pi\sigma^3$ and subtracting from 1,

$$f=\frac{r_1^3\zeta^3}{r_1^3-\sigma^3}\left[\frac{1}{\zeta^3}+\frac{1}{2}\frac{\sigma^3}{r_1^3\sigma^3}-\frac{16}{5}\right.$$

$$\left.+\frac{9}{5}\frac{r_1\zeta}{\sigma}-\frac{1}{10}\frac{r_1^3\zeta^3}{\sigma^3}\right], \tag{24}$$

where, of course, r_1 is to be determined by Eq. (22). However, before r_1 is determined, m must be found, and m will be a function of v. For the random close-packed arrangement we have rounded off m as 10.5. This gives by Eq. (20) an expansion in v of 14.3 percent over the cubic close-packed, which agrees well with Section 2. It may also be readily verified that when v is very large, so that σ^3 is negligible, Eqs. (16) and (24) coincide. Hence we may say that the result found for the dilute gas is equivalent to assuming that there are 1.6 nearest neighbors. In between these conditions m should have intermediate values, and we shall use a system of interpolation to determine them. The essence of the situation is that in the dilute gas the probability of the overlapping of the exclusion spheres of a given pair of molecules is independent of the other molecules, while in the concentrated gas the total amount of overlapping approaches a sort of saturation. The one state, which is equivalent to setting $m=1.6$, is dependent on the fact that in that state the overlap is small and $f=1$, while the other state, equivalent to setting $m=10.5$, results from the overlap being large, $f=0$. It seems reasonable to get m by linear interpolation with respect to f, i.e., by setting

$$m=1.6+(10.5-1.6)(1-f). \tag{25}$$

We then proceed as follows. From Eq. (24) we get f as a function of r_1/σ. By Eq. (25) we get m as a function of f and hence of r_1/σ. We then use Eq. (22) inversely, i.e., we find v/σ^3 as a function of r_1/σ. This, then, yields a relation between f and v (the latter in units σ^3), which is what is desired. This can be expressed as a relation between f and θ, which is exhibited graphically as the lowest curve in Fig. 3.

We may now proceed, by means of a consideration of some of the properties of Eq. (14), to get further evidence as to the validity of this

[22] Actually this is an approximate view of the situation, for it implies that the next nearest neighbors reduce f to zero by holding all the m nearest neighbors against the central molecule. Of course, it is not true that all the surrounding molecules actually touch the central molecule in the state of equilibrium; yet f is effectively zero because the packing is such that the amount of free space is not reduced by moving an average molecule.

[23] Compare O. K. Rice, J. Chem. Phys. **7**, 136, 883 (1939).

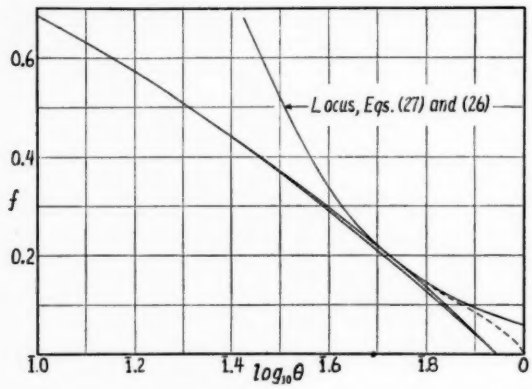

FIG. 3.

curve. We may write Eq. (14) in the form

$$\log_{10}(y-1)=\log_{10}x+0.434\times\tfrac{5}{8}fxy. \quad (26)$$

If the left-hand side of Eq. (26) is plotted as a function of y, we get the heavy curve shown in Fig. 4. If f is known as a function of v, the right-hand side of Eq. (26) can be plotted as a function of y for any value of $x=b/v$, giving a straight line, such as those shown in Fig. 4. These straight lines intersect the curve either in two points, in one point of tangency, or in none at all. It is quite evident that when v is very large and x is very small, so that the last term of Eq. (26) amounts to a correction term, and y is nearly equal to 1, the intersection giving the lower value of y is the correct one. On the other hand, v approaches a limiting smallest value and x accordingly a limiting highest value, while f approaches zero. As this happens, it is clear that the low intersection remains finite, but the high intersection approaches infinity. Since y must approach infinity, the high intersection is to be used in this case. It, therefore, appears that as x increases the straight line represented by the right-hand side of Eq. (26) must eventually become tangent to the curve, this marking the point at which the change in our choice of solution of Eq. (26) occurs. This suggests that we study the conditions of tangency.

At the point of tangency the slopes of the two sides of Eq. (26) must be equal; therefore

$$(y-1)^{-1}=\tfrac{5}{8}fx. \quad (27)$$

At the same time Eq. (26) must hold. If we eliminate y between Eqs. (26) and (27) we obtain a locus of f against x (or, equivalently, f against θ). This locus is exhibited in Fig. 3.

Now, if the straight line determined by the right-hand side of Eq. (26) for a specified value of x or θ is tangent to the curve of the left-hand side, this obviously corresponds to the largest possible value of f for the given value of x or θ. Hence the true curve for f *vs.* θ must lie nowhere above the locus determined by Eqs. (26) and (27). On the other hand, it must touch that locus at one point. It is seen that the curve based on the linear interpolation for m barely misses the locus. We have, therefore, made a very slight correction as indicated in Fig. 3. That the correction is so very slight may, of course, be to some extent fortuitous, but there does not seem to be much possible leeway for the corrected curve. Using the latter to determine f as a function of x, we have obtained graphical solutions of Eq. (26) in the manner indicated in Fig. 4. The circled points of intersection in Fig. 4 are shown on curve I of Fig. 5, after converting x to θ. This curve, we believe, gives the equation of state of the gas of hard elastic spheres with a considerable degree of accuracy, or at least would give it if it actually went over to the random close-packed arrangement at small volumes. The curve for y against $\log\theta$ is quite insensitive to the exact form of Eq. (25) up to $\log\theta=\bar{1}.4$ or $\bar{1}.5$. It is sensitive near the point of tangency, but in this region Fig. 3 appears to leave little doubt as to the proper choice of f.

It is, however, most likely that if we slowly compressed a gas of hard elastic spheres we would

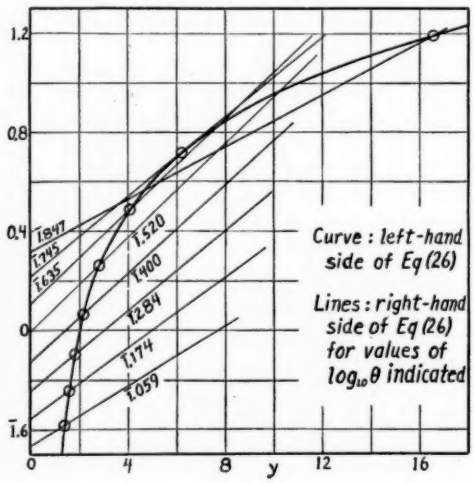

FIG. 4.

arrive, not at the random close-packed arrangement, but at the cubic (or, what is essentially equivalent, the hexagonal) close-packed arrangement. At very small volumes, the equation of state of the latter can be calculated from the partition function, Eq. (2), with Eq. (3), which gives[24]

$$y=(1-\theta^{\frac{1}{2}})^{-1}. \tag{28}$$

This is shown as curve II in Fig. 5, the corresponding values of f to $\log\theta=\bar{1}.8$ being shown as the broken curve in Fig. 3. In order to complete the equation of state we must find a means to join curve I at large volumes to curve II at small volumes; this will be done by consideration of the entropy.

In the case of hard elastic spheres, where the accessible regions of the phase space are independent of temperature, f must depend only on v. y, therefore, is independent of temperature. We may thus write, since $y=pV/RT$,

$$(\partial S/\partial V)_T=(\partial p/\partial T)_V=Ry/V. \tag{29}$$

y in Fig. 5, therefore, gives us $R^{-1}\partial S/\partial \ln V$ or $-R^{-1}\partial S/\partial \ln\theta$ directly. Integration from $\log\theta=-\infty$ to very small values of $\log\theta$, along the curve giving the true equation of state, including that part which connects curve I to curve II, should give us the change of entropy, which can also be calculated independently, since we know the entropy at both limits, that is, the entropy of a perfect gas on the one hand, and the entropy of the cubic close-packed system, through Eq. (2), on the other: The change of entropy from a volume v_2 in the perfect gas range, to v_1 in the cubic close-packed range, is

$$\Delta S=-R\ln[v_2/(e^2v_1)(1-\theta^{\frac{1}{2}})^3], \tag{30}$$

for Eq. (2) would apply to a perfect gas if the $(1-\theta^{\frac{1}{2}})$ factor were set equal to 1, and if Q contained a factor of e instead of e^3.

Curve I of Fig. 5 is empirically very closely reproduced up to the point at which it crosses curve II by

$$y=1+2.962\theta+5.48\theta^2+21.3\theta^4. \tag{31}$$

Logarithmic integration of this expression from a very large volume v_2 (small θ) to a volume v_1, corresponding to the point of crossing of curve I and curve II (this occurs at $\theta=0.43$) yields

$$\Delta S=-R\ln(v_2/v_1)-1.96R.$$

Evaluation from Eq. (30) gives

$$\Delta S=-R\ln(v_2/v_1)-2.22R,$$

which differs by $0.26R$ or 0.52 entropy unit. It is, therefore, seen that the curve connecting curve I to curve II, in order to give the true

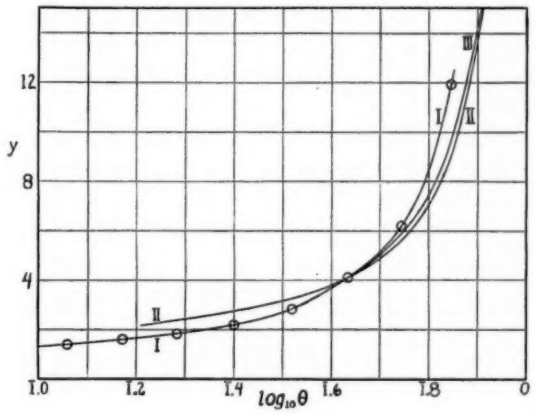

FIG. 5.

equation of state, will have to be some such curve as curve III of Fig. 5, which is so drawn that the entropy loss on following from the left first curve I, then curve III, then finally approaching curve II will conform to Eq. (30). This composite curve we propose as the most reasonable approximation for the equation of state of the gas of hard elastic spheres as it is compressed to a cubic close-packed solid. Though it is not derived in a strictly deductive manner, its self-consistency from a number of different points of view is so satisfactory as to be strongly in its favor. At fairly small volumes, it deviates remarkably little from curve II.

This curve differs somewhat from the curve I have previously suggested,[18] with less theoretical foundation. In the first place it follows Tonks' interpolated curve quite closely to $\log\theta=\bar{1}.4$ instead of only to $\bar{1}.0$. However, at greater values of $\log\theta$ it departs slightly more from Tonks' interpolation, rising, as noted, slightly above curve II, in order to maintain the validity of Eq. (30).

[24] Compare Tonks, reference 6, Eq. (32).

Curve III probably corresponds to a state of the system in which there are small groups of atoms in essentially a cubic close-packed structure, though the system as a whole is disordered. On compression of the gas, these groups increase in size and number. They enable the system to avoid the high pressures of curve I, but do not bring it all the way down to the pressures indicated by curve II until, at the very smallest volumes, complete order is produced. Their presence makes possible transition from a disordered to an ordered state.

4. THE PARTITION FUNCTION FOR A SIMPLE LIQUID

In the light of the above discussion of idealized systems, we now wish to formulate a partition function which can be applied with some degree of approximation to actual monatomic[25] liquids of the rare-gas type. There seems to be every reason to believe that a considerable degree of disorder exists in such liquids and that there is a variety of configurations with the same energy. This would indicate that a certain portion of the energy of motion may be described as translational; on the other hand, the forces between atoms in a real liquid are strong, and to some considerable extent the motion will resemble that in solids. We may thus say that the motion is in part solid-like, and in part gas-like. Of course, this is nothing new, and has been recognized in most theories of liquids. However, it is believed that we can lay down certain principles regarding the way in which these two types of motion must be combined, and obtain a partition function which can be better understood, in detail, in terms of these general principles than those previously used.

The first question to be settled is whether the degrees of freedom can be divided into two classes, some translational and some vibrational, or whether it is necessary to consider each degree of freedom as in part translational and in part vibrational.

The first idea has been considered in a somewhat special form by Brillouin[26] and Lucas,[27] and can be formulated in a very attractive way. Since the motion of the molecules of a liquid is a cooperative affair, as in the case of the solid, we naturally assume that there are certain normal modes of motion. Some of these would be oscillations of the usual type; others, however, would be oscillations of frequency zero, namely, translations of a complicated kind, involving the cooperative motion of numbers of atoms. The characteristic feature of the translations is that they are force-free motions which include motions which stir the atoms around, producing, perhaps, exchanges of position without altering interatomic distances, at least on the average; free rotations of groups of atoms would be a special case, and, in fact, the case visualized by Lucas. Attractive as this idea seems to be, I believe that it leads to difficulties.

Let us consider the motion, according to the picture just described, when the translational degrees of freedom are not excited. In this case, the addition of all the normal modes of motion results in each atom vibrating in the field of its neighbors without changing its relative position with respect to its neighbors. When the translational degrees of freedom are excited, this picture will not be greatly altered in the length of time required for the average vibration; i.e., the surroundings of any given atom will not appreciably change in this time. If the surroundings of the average atom did change appreciably in this time it would mean that the individual modes of motion contained an element of both translation and vibration, whereas we have postulated that these constitute separate modes of motion.

Let us now consider the analogy in the case of hard elastic spheres in a nearly close-packed random arrangement. Of course, strictly speaking, there would be no vibrational motion in this case, but analogous to the vibrational degrees of freedom would be short range motions of the spheres bounded by points of collision with neighboring spheres, without shift of relative position, while longer range shifts of position and exchanges of neighbors would correspond to the translational modes of motion of the real liquid. There would be a rapid change in entropy with volume as we approached the close-packed random arrangement, because of the relatively

[25] The words "atom" and "molecule" are used interchangeably.
[26] L. Brillouin, J. de phys. et rad. **7**, 153 (1936).
[27] R. Lucas, J. de phys. et rad. **8**, 410 (1937).

great change in the free path corresponding to the "vibrational" degrees of freedom, and a large increase of pressure as the system contracted toward the random close-packed arrangement. This would correspond to a system on curve I in Fig. 5, which is in itself an argument against it.

Actually, it seems inevitable that at larger volumes there will be considerable mixing and free exchange of positions of the molecules, and hence contributions of both a translational and "vibrational" type in these individual motions. As we have seen, we may in general expect the system to follow a composite of curves I, III, and II, there being a tendency, as the system is compressed, for the atoms, at first in small groups, to take up the true close-packed arrangement. The reason that some atoms do this is that it allows more room for other atoms to maintain their free individual motions, which combine the properties of "vibration" and translation. This means that the free path of individual atoms is greater than one would predict from "vibrational" modes of motion, and that the process of exchange of positions of neighbors contributes to the individual free path, and so takes place, or at least gets well started, in a time comparable to the average time of vibration. It is true, of course, that there is a gradual loss of translational motion, and that the atoms in the close-packed groups lose it more rapidly than the others. But it is questionable whether the lifetime of such a group is so very much greater than the average period of vibration. Under these circumstances, it seems to me that it will be preferable to use what amounts to an analogy of the Einstein theory of the solid, in which the motion of each atom represents an average of what goes on in the liquid.

It will be interesting to see what this point of view leads to in the picture of Brillouin and Lucas, in which the force-free modes of motion are assumed to have a rotatory character. We can suppose the liquid to be divided up into groups of atoms, each group having internal vibrations and being free to rotate. These groups must be fairly small, not over three or four atoms, in order for there to be enough rotational degrees of freedom to appreciably affect the properties of the liquid. If such a group can rotate freely and as a whole for a time greater than the average period of vibration, then it is legitimate to assume normal vibrational modes of motion and other normal rotatory modes of motion. If the group splits up, or cannot rotate freely over a period of this order of magnitude, then the different types of motion must be combined in each degree of freedom. It is this latter alternative which we believe to be the correct one.

We may suppose that the atoms will have a motion similar in some respects to that of an atom moving in a potential field such as shown in Fig. 6. In the figure the potential for a harmonic oscillation has been split in two, and a section of zero potential, corresponding to translation, inserted in between from point A to point B. This type of potential has been considered several times before[28] and it is obvious that the partition function will be the sum of the partition functions of the harmonic oscillator and the one-dimensional "particle-in-a-box" which is free to move between points A and B. This would give for the partition function per atom $T/\Theta+(2\pi mkT/h^2)^{\frac{1}{2}}x$, where Θ is the characteristic temperature of the oscillator and x is the distance between A and B.

However, this expression must be modified in several ways. In order to see how these modifications are to be made, it will be best to proceed from the partition function for the case of hard elastic spheres. From the above discussion of this case, it appears that the partition function given by Eq. (2) will be valid, at least within a few tenths of an entropy unit, even after the volume has become sufficiently great so that the arrangement of the atoms appears to be quite random. Thus it is as if each atom had an average free motion in a given direction for a distance of $v^{\frac{1}{3}}(1-\theta^{\frac{1}{3}})=2^{-\frac{1}{2}}a(1-\theta^{\frac{1}{3}})=2^{-\frac{1}{2}}(a-\sigma)$, where a is the smallest interatomic distance (distance between equilibrium positions of nearest neighbors) for a cubic close-packed lattice of molecular volume v. The factor e per degree of freedom takes care of the communal entropy. In the real liquid some of this free space in not truly free, i.e., some of the motion takes place in a force field. Let us suppose that the part of the motion which is completely free corresponds to the partition function (for *one degree of freedom*) $(2\pi mkT/h^2)^{\frac{1}{2}}2^{-\frac{1}{2}}e(a-a_0)$.

[28] See, e.g., reference 5.

Then, effectively, we may say that for distances smaller than a_0 we are in the field of force.

It seems reasonable to suppose that the contribution to the partition function per degree of freedom due to the motion in the field of force can be given by $e^{\frac{1}{2}}T/\Theta(a_0)$, where $\Theta(a_0)$ is the Debye characteristic temperature for a cubic close-packed lattice with the smallest interatomic distance a_0. In this form, this part of the partition function carries with it its own characteristic contribution to the communal entropy.

However, a little reflection will show that this term still needs some modification, for, in the liquid, the atoms are acting as individuals rather than as elements in a lattice. As has been pointed out above, the value of Θ in a crystal is increased by the presence of the atoms in rows adjacent to one in which the particular vibration we may be interested in occurs.* In fact, our previous calculations[14] indicate that the force resisting displacement of a given atom from its position of equilibrium is, at least to a first approximation, just twice as great in a cubic close-packed lattice, and, corresponding thereto, that Θ is $2^{\frac{1}{2}}$ times as great, as if only the atoms in a single row were effective. This result depends upon the assumption that the calculation of the frequency can be handled by the method of small vibrations, which, as will be shown in a subsequent article, may not be a very good assumption; still it seems likely that the factor $2^{\frac{1}{2}}$ is a reasonably good approximation.

The factor $2^{\frac{1}{2}}$ is closely connected with the arrangement of the side atoms in fixed positions. In the case of the liquid the position of the side atoms is not fixed with respect to any pair of "colliding" atoms which we may consider. The side atoms may be at distances at which repulsion occurs, or they may be at slightly larger distances at which attraction occurs. Furthermore, as a given pair of atoms approach each other, the side atoms can adjust themselves with some degree of ease to the new situation. It, therefore, appears that the factor $2^{\frac{1}{2}}$ should not appear in the case of the liquid;[29] or, if we take $\Theta(a_0)$ as the

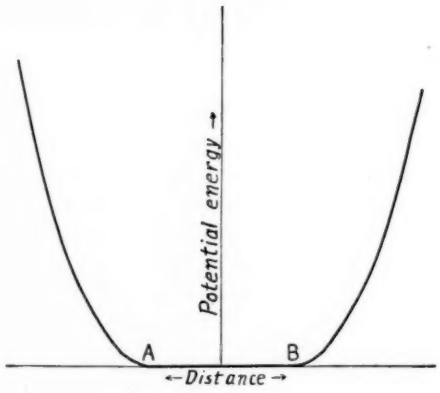

FIG. 6.

characteristic temperature of the solid lattice, it should be divided by $2^{\frac{1}{2}}$. But since the side atoms still have the same space-filling property that they have in the case of the hard elastic spheres, the partition function should be divided by a factor, which as a first approximation may be taken as the same factor which divides the free length in the latter case, namely $2^{\frac{1}{2}}$. Thus the vibrational contribution to the partition function becomes

$$e^{\frac{1}{2}}T/\Theta(a_0)(2^{\frac{1}{2}}/2^{\frac{1}{2}}) = (2e)^{\frac{1}{2}}T/\Theta(a_0).$$

We, therefore, propose as the partition function of a monatomic liquid, per atom, the following expression:

$$Q = [(2e)^{\frac{1}{2}}T/\Theta(a_0) + (2\pi mkT/h^2)^{\frac{1}{2}}2^{-\frac{1}{2}}e(a-a_0)]^3, \quad (32)$$

the value of a_0 remaining to be determined. This expression, of course, gives only that portion of the partition function which may be referred to the thermal energy of the system. Of course, some potential energy is included in the term, thermal energy, namely, that part of the potential energy which varies with the temperature when the parameters, a and a_0 are held fixed. For the work function (Helmholtz free energy) of the system,

* Figure 2 above may be used to illustrate this point. Atoms like E and D, as well as atoms like C and B, contribute the force on atom A when undergoing the displacement shown.

[29] Since we consider here the collision of a single pair of molecules as being more or less unaffected by their other neighbors, and since in a row of atoms, each atom is always under the influence of two neighbors, it might be supposed that Θ for a liquid would be less by a factor $2^{\frac{1}{2}}$ than even the Θ for a single row of atoms. However, if certain interatomic distances become smaller, an equal number must become correspondingly larger, if the density is to remain fixed. It, therefore, appears that when one atom approaches a neighbor, we cannot neglect the effect of the opposite atom, even though we neglect the effect of the side atoms.

we may write

$$A = -RT \ln Q + E_p, \tag{33}$$

where E_p is a function of a and a_0 and is the potential energy which the system would have if it were possible for it to approach absolute zero and still obey the classical statistics. In order for this picture to be self-consistent, E_p must not vary with the temperature explicitly. However, even if the condition of constant volume is imposed, which means constant a, E_p may depend on the temperature through a_0 if it varies. We must, in general, write

$$\begin{aligned} S = -(\partial A/\partial T)_V &= R \ln Q \\ &+ (RT/Q)[(\partial Q/\partial T)_{a,a_0} \\ &+ (\partial Q/\partial a_0)_{a,T}(\partial a_0/\partial T)_a] \\ &- (\partial E_p/\partial a_0)_a(\partial a_0/\partial T)_a. \end{aligned} \tag{34}$$

There are now two ways in which we may regard the quantity a_0. The first is to consider a_0 as an additional parameter, which may, in our imagination, be varied at will. Thus we may suppose various geometrical configurations at constant volume, differing in coordination number. The more the arrangement deviates from cubic close-packing, the smaller the coordination number and the smaller the nearest-neighbor distance, simultaneously, must become. This will be reflected in a decrease in a_0, as the smaller the interatomic distance the greater the free space between atoms and, therefore, the greater the translational part of the partition function. The thermodynamic equilibrium will occur, at any given temperature and atomic volume, when $-A$ is a maximum, i.e., when

$$(RT/Q)(\partial Q/\partial a_0)_{a,T} - (\partial E_p/\partial a_0)_a = 0. \tag{35}$$

Combining this with Eq. (34) we get

$$S = R \ln Q + (RT/Q)(\partial Q/\partial T)_{a,a_0}. \tag{36}$$

The other possible point of view is to suppose that a_0 is purely a geometrical quantity, determined by the volume, the size of the atoms, and the forces between them. This point of view is, perhaps, supported by the considerations in the case of the hard elastic spheres, in which no mention is made of apparent coordination number, but in which it appears that full use of all the possible positions of the atoms must be made in calculation of the partition function or the phase integral. Of course, the situation is more complicated in the case where the atoms exert the usual type of force upon each other, and we may question whether, at given a, the value of a_0 is independent of T. At first sight it might appear that this is not the case, because it would be supposed that, at higher temperatures where some of the atoms are closer together because the positional fluctuations are higher, it would be possible to find a greater range of positions over which the energy would be constant, and that, therefore, $a - a_0$ should be smaller. However, this would mean that the translational part of the energy would actually take on the character of a vibration, for the characteristic of a vibrational motion is that it has a greater range the higher the temperature. The aim of the expression (32) is to divide up the contributions to the partition function into a translational and a vibrational part; if this is to be possible, it should be possible to find some a_0 which will not vary with the temperature. It results in the entropy again being given by Eq. (36).

We may look at this matter in a little different way. The first term in the bracket in Eq. (32) is equivalent to another term like the second one, except that the equivalent free distance (corresponding to $a - a_0$ in the second term) depends upon the temperature. In other words, it is like a collection of hard spheres, but the radius of these spheres depends upon the temperature. The effect of this dependence of the effective radius of the "hard" sphere on the temperature is less the greater the volume; hence there must be a term, like the second in the bracket, which has a lesser dependence on temperature. It is not to be denied that the statement that a_0 depends only on a is an assumption; it is seen, however, to be qualitatively reasonable, and is the simplest assumption that can be made in actually applying the theory to experimental data.

In previously published work,[4] I have adhered to the first of the above propositions, namely, that a_0 is a parameter. Actually I used the coordination number as the parameter, which is equivalent. This work ran into some difficulties in unpublished calculations, which I could attribute in part to inability to take some of the geometrical factors into account. This would seem to point to the preferability of the point of view that a_0 is

a function of a, determined by the geometry of the system. Recently, I have had some success in coordinating those properties of liquid argon which are connected with the entropy, and in relating them to the properties of solid argon, using this latter point of view. It is planned to publish these results in a future communication.

APPENDIX. FLUCTUATIONS IN A ROW OF HARD ELASTIC SPHERES

We consider a row of N spheres of diameter σ on a line of length l, and select one whose fluctuations we wish to investigate. Assume there are N_1 spheres to the left of the selected sphere and N_2 to the right. We have

$$N_1+N_2+1=N.$$

The free space to the left of the selected sphere is l_1, and to the right is l_2. We have

$$l_1+l_2+\sigma=l.$$

There will be a position of maximum probability for the selected sphere, where the force exerted by the spheres to the left due to their thermal agitation is equal to the force exerted by spheres to the right. This is determined by setting these forces, which are given, respectively, by[30]

$$f_1=N_1kT/(1-\theta_{1,1})l_1$$
$$f_2=N_2kT/(1-\theta_{1,2})l_2$$

equal to each other. This position of maximum probability will not necessarily be the same as the average position; Tonks has shown that the average positions of the spheres are regularly spaced along the line. The position of maximum probability will, however, not be displaced from the average position by more than the greater of $(l/N)(1-\theta_1)/2N_1$ or $(l/N)(1-\theta_1)/2N_2$. If the selected sphere be given a displacement of Δl (assumed small compared to l_1 or l_2) from the position defined by setting $f_1=f_2=f_0$ (we shall hereafter designate this position by the subscript zero) we have

$$f_1=\frac{N_1kT}{(1-\theta_1)l_{1,0}+\Delta l}\backeq f_0\left(1-\frac{\Delta l}{l_{1,0}(1-\theta_1)}\right),$$
$$f_2=\frac{N_2kT}{(1-\theta_1)l_{2,0}-\Delta l}\backeq f_0\left(1+\frac{\Delta l}{l_{2,0}(1-\theta_1)}\right),$$
$$f_2-f_1=f_0(l-\sigma)\Delta l/(1-\theta_1)l_{1,0}l_{2,0}.$$

The amount of work necessary to effect the displacement will be

$$\int_0^{\Delta l}(f_2-f_1)d\Delta l=f_0(l-\sigma)(\Delta l)^2/2(1-\theta_1)l_{1,0}l_{2,0}.$$

The probability of a displacement Δl will, therefore, be given by

$$P=P_0\exp[-f_0(l-\sigma)(\Delta l)^2/2(1-\theta_1)l_{1,0}l_{2,0}kT],$$

where P_0 is the probability of a displacement of zero. Now

$$f_0=\frac{N_1kT}{(1-\theta_1)l_{1,0}}=\frac{N_2kT}{(1-\theta_1)l_{2,0}}$$
$$=\frac{(N_1+N_2)kT}{(1-\theta_1)(l_{1,0}+l_{2,0})}=\frac{(N-1)kT}{(1-\theta_1)(l-\sigma)}.$$

Hence

$$P=P_0\exp[-(N-1)(\Delta l)^2/2(1-\theta_1)^2l_{1,0}l_{2,0}],$$

which is Eq. (4). It should be noted that θ_1, in these equations is equal to $(N-1)\sigma/(l_{1,0}+l_{2,0})$ or $(N-1)\sigma/(l-\sigma)$ rather than $N\sigma/l$, which means that $1-\theta_1$ is equal to $(l-N\sigma)/(l-\sigma)$ instead of $(l-N\sigma)/l$. The free length per atom, for the N atoms, which is $(l-N\sigma)/N$, is, therefore, equal to $(1-\theta_1)(l-\sigma)/N$.

[30] See Tonks, reference 6, Eq. (15). Note that our $\theta_{1,1}=N_1\sigma/l_1$ and $\theta_{1,2}=N_2\sigma/l_2$. When $f_1=f_2$, then $\theta_{1,1}=\theta_{1,2}=\theta_1$.

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Discrimination in Mass Spectrometer Ion Sources

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An analysis is made of the collection and definition of a beam of ions by an ion source. It is found that the first slit of the source has no discriminating effect but the second slit does have. This is due to the fact that ions of certain values of initial energy, angle of velocity vector, and position of striking the plane of the first slit cannot get through the second one. An efficiency of collection of a source for ions of a certain initial energy is defined as the ratio of the number with that initial energy that get through the second slit to the number with that initial energy which get through the first slit. An expression for this efficiency is derived and it is applied to rather typical data to show how an abundance ratio obtained by taking the ratio of peak heights may be in error several percent. The method of measuring isotopic abundances is recommended wherein the focusing conditions are changed only by varying the magnetic analyzer field.

FOR some time it has been believed that it is possible for the accelerating slit system in a mass spectrometer ion source to discriminate between ions of different mass, i.e., to collect ions of one mass more effectively than those of another. This would lead to different values of the isotopic abundances measured with different instruments.

One possible source of discrimination is the fact that the solid angle of collection, i.e., the angle in which ions are collected, may vary from one ion to the next during a determination of isotopic abundances. It is the purpose of this paper to analyze the reason for this discrimination and to calculate the magnitude of its effect. The effect of this change of solid angle of collection on peak shape for ions from dissociating molecules has been considered by Hagstrum and Tate.[1]

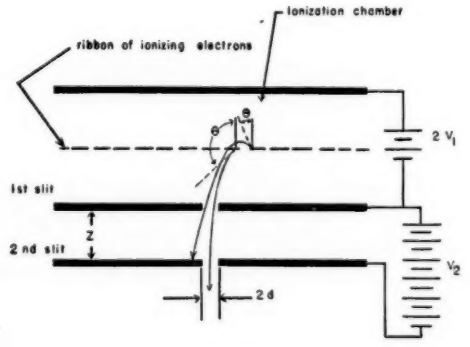

FIG. 1.

Let us consider an ion source such as shown schematically in Fig. 1 where the ions are formed by a beam of electrons coming into the ionization region parallel to the plane of the first slit. In this figure are shown two ions originating in the region of the electron beam with different values of θ, one ion being able to traverse the second slit and one not being able to. Let us further restrict ourselves to an ion source which is magnetic field free.[2] Since all ions are formed with an initial velocity (either thermal or due to dissociation energy, as for ions from molecules), let us denote this velocity by c and denote the angles of its vector by θ and Φ. Let us denote by c', θ', Φ' the corresponding quantities for the ion as it passes through the first slit, and by c'', θ'', Φ'', the corresponding quantities as it passes through the second slit. Let V_1 be the potential difference between the first slit and the position traversed by the electron beam. Let V_2 be the potential difference between the first and second slits. Let the separation between the first and second slits be z and the slit width in each case be $2d$. We shall consider an ion source in which no magnetic field is present, and we shall assume that the electric field is uniform both in the region above the first slit and in the region between the first and second slits.

If the area of the first slit is small compared to the area of the electron beam and if the first slit is located well away from any of the edges of the electron beam, it is clear that there can

[1] H. D. Hagstrum and J. T. Tate, Phys. Rev. **59**, 354 (1941).

[2] N. D. Coggeshall and E. B. Jordan, Rev. Sci. Inst. **14**, 125 (1943).

be no selective influence due to the first slit alone. For, consider ions of any mass, there will be created in the electron beam a definite number per unit area; and since the electric field is uniform, the number arriving per unit area on the plane of the first slit will be equal to this, so the number collected by the first slit is proportional only to its area and the number created per unit area in the electron beam.

The second slit, however, does have a selective influence as can be seen from Fig. 1. This is because only part of the ions going through the first slit get through the second slit and this fraction depends upon the initial velocity of the ions and upon the accelerating voltages used.

Let us consider ions of mass m. We shall denote by $\rho(c)$ the number of ions of mass m and initial velocity c which are created per second, per unit area in the electron beam. Now since the first slit gathers as many, per unit area, as are created per unit area in the electron beam we have:

$$f(\theta', \Phi', c')d\omega' = \rho(c)(d\omega/4\pi), \tag{1}$$

where $f(\theta', \Phi', c')$ is the number of ions of coordinates θ', Φ', and velocity c', contained within unit solid angle ω' at the plane of the first slit; $d\omega$ refers to solid angle in the electron beam. We assume that the ions have initial velocities randomly distributed. Using $d\Phi = d\Phi'$ and $c \sin\theta = c' \sin\theta'$, $f(\theta', \Phi', c')$ turns out to be:

$$f(\theta', \Phi', c') = \frac{\rho(c)}{2\pi} \frac{c'^2 \cos\theta'}{c(c^2 - c'^2 \sin^2\theta')^{\frac{1}{2}}}. \tag{2}$$

We may now evaluate the selective influence of the second slit by defining an efficiency of collection $p(c)$. We define $p(c)$ as being the ratio of ions of mass m and initial velocity c getting through the second slit to the number getting through the first slit. From previous consideration we know that this is equal also to the ratio of the number of ions of mass m and initial velocity c in the final ion beam to the number created in the electron beam in an area equal to the area of the first slit.

$$p(c) = \frac{\rho(c)A' - \int\int f(\theta', \Phi', c')d\omega' da'}{\rho(c)A'}, \tag{3}$$

where A' is the area of the first slit. The integral is integrated over those portions of solid angle ω', such that ions striking the first slit in those portions of solid angle do not get through the second slit; also it is integrated over the area of the slit.

In order to evaluate the above integral, let us consider the limiting values of θ', Φ' that an ion of initial velocity c may have at the first slit and still get through the second slit. Let an ion strike the first slit, at a distance s from one edge and with a given Φ' and initial velocity c. Then one limiting value of θ' must satisfy the following relationships:

$$s = \frac{c' \sin\bar{\theta}' \cos\Phi' z}{II_{Av}},$$

where H_{Av} is the average value of the component of the ion's velocity perpendicular to the planes of the slits, while the ion is between the first and second slits, if $V_2 \gg V_1$ as is usually the case, we may write $H_{Av} = c''/2$ since $2eV_2/m \gg c^2$, where c is initial thermal velocity or even dissociation velocity of a few volts.

This gives:

$$s = (2c'/c'') \sin\bar{\theta}' \cos\Phi' z. \tag{4}$$

The other limiting value of θ' is given by:

$$\bar{\theta}' = \sin^{-1}(c/c'), \tag{5}$$

which is the case when all the initial velocity c is parallel to the plane of the first slit. The limits of Φ' are:

$$\pm\cos^{-1}\frac{sc''}{2zc},$$

so $p(c)$ becomes, neglecting end effects:

$$p(c) = \frac{\rho(c)2Ld - f(c)}{\rho(c)2Ld}, \tag{6}$$

where L is the length of the slits and $f(c)$ is given by:

$$f(c) = \frac{2\rho(c)}{\pi} L \frac{c'^2}{c} \int_0^{2d} ds \int_0^{\cos^{-1}(sc''/2zc)} d\Phi' \times \int_{\sin^{-1}(sc''/2zc' \cos\Phi')}^{\sin^{-1}(c/c')} \frac{\cos\theta' \sin\theta' d\theta'}{(c^2 - c'^2 \sin^2\theta')^{\frac{1}{2}}}.$$

The factor 2 appearing in $f(c)$ is the alternative to setting up an additional integral where instead of having ds we have $d(2d-s)$, i.e., the integral to take care of ions having Φ' differing by 180° from the values considered.

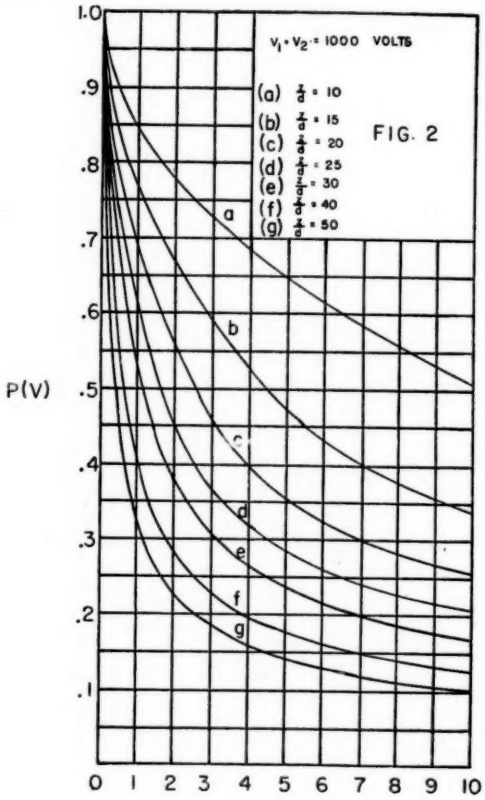

FIG. 2. Energy in electron volts.

Integrating with respect to θ' and inserting the limits we obtain:

$$f(c)=\frac{2\rho(c)L}{\pi}\int_0^{2d}\int_0^{\cos^{-1}(sc''/2zc)}\times\left(1-\left(\frac{sc''}{2zc}\right)^2\frac{1}{\cos^2\Phi'}\right)^{\frac{1}{2}}d\Phi' ds.$$

Suppose we let $(sc''/2zc)=a$

$$f(c)=\frac{2\rho(c)L}{\pi}\int_0^{2d}\int_0^{\cos^{-1}a}\times\frac{1}{\cos\Phi'}(\cos^2\Phi'-a^2)^{\frac{1}{2}}d\Phi' ds.$$

Suppose we next let

$$\frac{\cos^2\Phi'-a^2}{1-\cos^2\Phi'}=v^2;$$

we obtain:

$$f(c)=\frac{2\rho(c)L}{\pi}\int_0^{2d}\int_0^{\infty}\frac{v^2(1-a^2)dvds}{(1+v^2)(v^2+a^2)}$$

which can be integrated by partial fractions to yield:

$$f(c)=\rho(c)L\int_0^{2d}(1-a)ds; \tag{7}$$

or using value of a and inserting in (7) we get:

$$f(c)=2\rho(c)Ld\left(1-\frac{d}{z}\frac{1}{2}\frac{c''}{c}\right). \tag{8}$$

Now this expression for $f(c)$ has been derived for values of c such that the second slit was operative in cutting out ions regardless of where they struck the first slit. However, for small values of c there are regions of the first slit where the ions may strike and be free of the discriminating effects of the second slit. For such values of c the integral $f(c)$ becomes

$$f(c)=\rho(c)L\int_0^{\bar{s}}(1-a)ds \quad \text{where} \quad \bar{s}=\frac{2zc}{c''}$$

or

$$f(c)=\rho(c)Lz(c/c''). \tag{9}$$

The value of c for which $f(c)$ changes from form (8) to form (9) is of course given by $d=zc/c''$, i.e., it will be given by the root of the equation:

$$d\left(c^2+\frac{2e}{m}(V_1+V_2)\right)^{\frac{1}{2}}=zc.$$

Let us call this transition value $\bar{c}$. Then our efficiency of collection is given by:

$$p(c)=1-[(1/2)(z/d)(c/c'')] \quad \text{for} \quad c<\bar{c}, \tag{10}$$

$$p(c)=[(1/2)(d/z)(c''/c)] \quad \text{for} \quad c>\bar{c}. \tag{11}$$

Or if we express the initial velocities in terms of electron volts of energy V we obtain:

$$p(V)=1-\frac{z}{2d}\left(\frac{V}{V+V_1+V_2}\right)^{\frac{1}{2}} \quad \text{for} \quad V<\bar{V}, \tag{12}$$

$$p(V)=\frac{d}{2z}\left(\frac{V+V_1+V_2}{V}\right)^{\frac{1}{2}} \quad \text{for} \quad V>\bar{V}. \tag{13}$$

As they should, the two expressions for $p(V)$ agree in value and slope for $V=\bar{V}$. Graphs of $p(V)$ for various values of z/d and for $V_1+V_2=1000$ volts may be seen in Fig. 2. These curves agree in general over-all characteristics with those obtained by Hagstrum and Tate.[1] However, in the important region of small initial velocities the curves differ radically.

As the function $p(V)$ is independent of the mass of the ion being collected, true values of isotopic abundance ratios should be obtained if

all the ions are collected with voltage conditions remaining the same in the ion source. The only way this can be realized, of course, is by bringing first one ion beam and then another into focus by varying the magnetic field only.

Let us assume that the ions when formed from a monatomic gas will have a Maxwellian energy distribution. Then the density of ions of isotope M_α, in the path of the electron beam, as a function of energy will be

$$\rho_\alpha(V)dV = Kp_\alpha A\epsilon^{-eV/300kT}V^{\frac{1}{2}}dV, \qquad (14)$$

where p_α = partial pressure of isotope M_α

$$A = \pi N\left(\frac{e}{\pi kT}\right)^{\frac{3}{2}}\frac{1}{(300)^{\frac{1}{2}}},$$

V = energy in electron volts, N = total density of atoms of all isotopes, e = electronic charge, m_α = mass of isotope M_α.

K represents the fraction of atoms present in electron beam which are ionized; i.e., it represents ionization efficiency. We shall assume K to be the same for all isotopes of same element.

The intensity of the ion current for isotope M_α will then be proportional to I_α where:

$$I_\alpha = \int_0^\infty \rho_\alpha(V)P(V)dV.$$

Since $\epsilon^{-eV/300kT} \ll 1$ for V of the order 1 volt and for temperatures of the order of 500°C we may use the expression for $P(V)$ which was obtained for small values of V, i.e., (12):

$$I_\alpha = Kp_\alpha A\int_0^\infty \epsilon^{-eV/300kT}V^{\frac{1}{2}} \times\left(1-\frac{z}{2d}\left[\frac{V}{V_1+V_2+V}\right]^{\frac{1}{2}}\right)dV.$$

Since for operating conditions $V \ll (V_1+V_2)$ we have

$$I_\alpha = Kp_\alpha A\int_0^\infty \epsilon^{-eV/300kT}V^{\frac{1}{2}}(1-g_\alpha V^{\frac{1}{2}})dV,$$

where

$$g_\alpha = \frac{1}{2}\frac{1}{(V_1+V_2)^{\frac{1}{2}}}\frac{z}{d},$$

$$I_\alpha = Kp_\alpha A\left\{\frac{1}{2}\left(\frac{(300)^3\pi k^3T^3}{e^3}\right)^{\frac{1}{2}} - g_\alpha\left(\frac{300kT}{e}\right)^2\right\}, \qquad (15)$$

$$I_\alpha = p_\alpha\bar{A}\left\{\frac{1}{2}\frac{\pi e}{300kT} - g_\alpha\right\},$$

where

$$\bar{A} = KA\left(\frac{300kT}{e}\right)^2.$$

Suppose $T = 450°\text{K}$, then

$$I_\alpha = p_\alpha\bar{A}\{4.46 - g_\alpha\}. \qquad (16)$$

By a similar calculation we can show that the ion beam intensity of an isotope M_b would be proportional to I_b where:

$$I_b = p_b\bar{A}\{4.46 - g_b\}.$$

Using the usual practice of taking ratios of peak heights to get isotopic abundances, the observed abundance ratio of isotope M_α to M_b would be:

$$I_\alpha/I_b = [(p_a)(4.46-g_a)/(p_b)(4.46-g_b)]$$

instead of p_α/p_b which would be the true abundance ratio.

As a test of the order of magnitude of the error introduced by such discrimination let us consider the neon isotopes Ne^{20} and Ne^{22}. Let us suppose in our instrument that the ions are focused for a path with radius of curvature 5″. Further, let us suppose that we have a magnetic field of 800 gauss and the two slits in the ion source are $\frac{1}{4}$″ apart and 0.007″ in width. It would be necessary to accelerate the Ne^{20} ions through a voltage $V_1+V_2=965$ volts and the Ne^{22} ions through $V_1+V_2=877$ volts. Using these values in our expression for I_α/I_b we obtain:

$$\frac{I(Ne^{20})}{I(Ne^{22})} = \frac{p(Ne^{20})}{p(Ne^{22})}\times 1.02.$$

In other words, the value obtained by taking a ratio of the peak heights would be 2 percent in error. This is much larger than the usual experimental error and it is certainly outside the limits of accuracy some investigators claim.

DISCUSSION

In Fig. 2 are to be seen graphs for $P(V)$ for values of V up to 10 volts and for $V_1+V_2=1000$ volts with different values of z/d. As can be seen from them, the smaller the value of z/d the less discrimination an ion source will have;

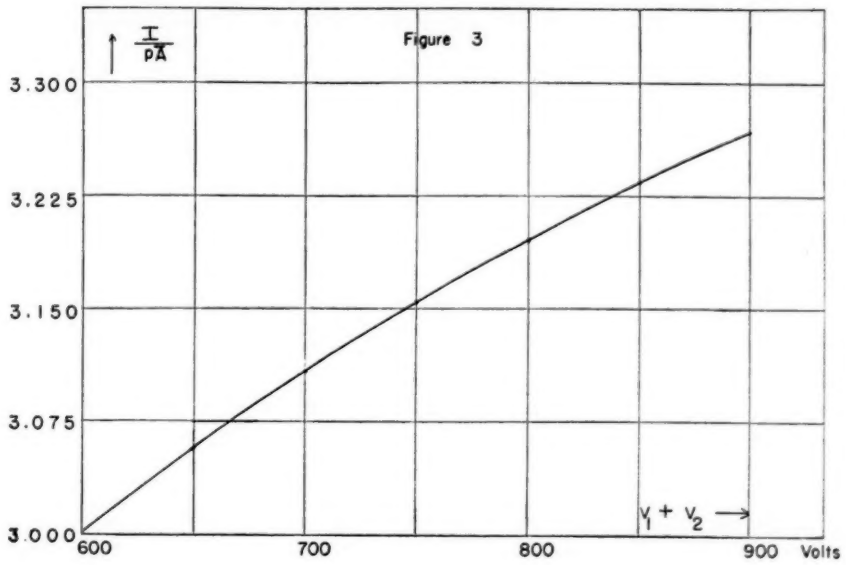

FIG. 3.

that is, the less the separation between slits as compared to slit width. When working with ions originating in dissociation processes we would expect the characteristics of the ion source strongly to affect the shape of the peaks. The dependence is through the $P(V)$ curve and is discussed by Hagstrum and Tate.[1] From our Fig. 2 we can see that the $P(V)$ curve would strongly affect the peak shape due to the steepness of the curve for energy values of the order of one electron volt.

It is to be remembered that the analysis above is for a rather simplified ion source, i.e., one in which the electric fields are uniform and one which is free of a magnetic field. The latter condition is not hard to meet but the first condition is one which in practice could only be approximated. This is because of the fringing of the fields near the slits and the penetration of the strong field into the weaker field region through the first slit.

In view of the simplified ion source analyzed, the numerical results and the expression for $P(V)$ should not be taken as exact for any ion source. However, it is reasonable to believe that the qualitative implications are true and that the expressions obtained are good as a first approximation for any actual case. Actually it is expected that the discrimination would be worse since the penetration of the high voltage field through the first slit can give the ions an added amount of velocity in a direction parallel to the planes of the slits and in this way decrease their chances of getting through the second slit. However, the method recommended above for getting abundance ratios, i.e., focusing by varying the magnetic field only, would be expected to give the best answer as this would not vary the discrimination for the different ions as their peaks were measured.

From Eq. (16) one would expect the peak height of any ion to grow if it were focused using progressively higher values for V_1+V_2. This is illustrated in Fig. 3. In this figure not the peak height is plotted, but a quantity to which the peak height is proportional, namely, I/pA. In the plotting directly of the peak the slope would be greater or less depending upon units used. As may be seen the curve, which is for any ion focused for values of V_1+V_2 between 600 and 900 volts, is slightly concave downwards but could be represented quite accurately by a straight line.

It would be desirable to have a similar analysis for the type of ion source in which there is a magnetic field present in the ion source, usually for the purpose of aligning the ionizing electrons. Some discussion has been made of this type of source[3] but the amount of discrimination is not calculated.

[3] E. B. Jordan and N. D. Coggeshall, J. App. Phys. **13**, 539 (1942).

Viscosity and Structure of Pure Hydrocarbons

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The two constants, A and E, of a two-constant equation, $\varphi = A \exp(-E/kT)$, for the fluidity φ, are tabulated for a number of hydrocarbons. The variations of these constants with structure are discussed.

INTRODUCTION

A NUMBER of investigators, among whom may be mentioned Thorpe and Rodger,[1] Mabery and Mathews,[2] Wilson and Allibone,[3] Spilker,[4] Hugel,[5] and Mikeska,[6] have investigated the effect on viscosity of various structural relationships. However, all these workers attached too much importance to the viscosity at some arbitrary temperature, such as room temperature, the boiling point, or the melting point. There has as yet been no attempt to eliminate completely the temperature variable in such investigations.

Kauzmann and Eyring[7] have shown that the viscosity η of a liquid can be expressed by the equation:

$$\eta = \frac{\lambda_1 h}{\lambda_2 \lambda_3 \lambda^2} e^{-\Delta S^{\mp}/R} e^{\Delta H^{\mp}/RT},$$

where λ_1 is the distance between moving layers of molecules; λ_2 is the dimension of the unit of flow, i.e., the molecule, in the direction of flow; λ_3 is the dimension of the unit of flow perpendicular to λ_1 and λ_2; λ is the distance moved by the unit of flow in passing over a potential energy barrier; $\Delta H^{\mp}$ is the activation energy per mole, i.e., the energy required for a molecule to reach the top of a potential energy barrier; $\Delta S^{\mp}$ is the corresponding entropy of activation; T is the temperature; and R is the gas constant. If we write the equation in terms of fluidity ϕ, since

$$\phi = \frac{1}{\eta},$$

we have

$$\phi = \frac{\lambda_2 \lambda_3 \lambda^2}{\lambda_1 h} e^{\Delta S^{\mp}/R} e^{-\Delta H^{\mp}/RT}.$$

Since $(\lambda_2 \lambda_3 \lambda^2/\lambda_1) \sim (V/N)$, the molecular volume, the equation may be simplified to:

$$\phi = \frac{V}{Nh} e^{\Delta S^{\mp}/R} e^{-\Delta H^{\mp}/RT}.$$

Since V and $\Delta S^{\mp}$ do not vary greatly with temperature, this equation is of the form suggested by Arrhenius:[8]

$$\phi = A^{-E/RT}.*$$

If we consider A and E constants (experimental results justify this assumption, at least to within the experimental error of most viscosity measurements), these two quantities can be used to compare viscosities of various liquids. Values of E and A have been calculated for 44 hydrocarbons by *the method of least squares* using viscosity data reported in the literature. The results are tabulated in Table I.

VALIDITY OF THE ARRHENIUS EQUATION

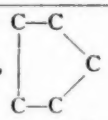
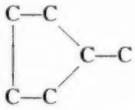
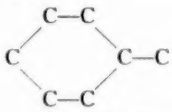
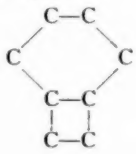
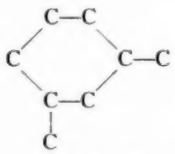
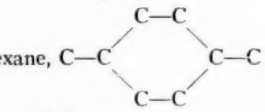
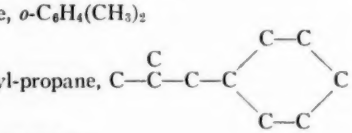
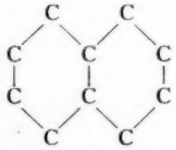
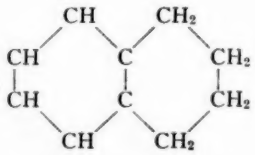
If A and E are constant, a straight line should be obtained when $\log \phi$ is plotted against $1/T$. Actually there is a very slight curvature, but in no case does $\log_{10} \phi$ vary from the calculated value by more than 0.027, corresponding to a 6.5 percent error in ϕ. Differences of more than 0.015 in $\log \phi$ (3.5 percent error in 0) are rare

[1] T. E. Thorpe and J. F. Rodger, Phil. Trans. **A185**, 397 (1894).
[2] C. F. Mabery and J. H. Mathews, J. Am. Chem. Soc. **30**, 992 (1908).
[3] W. J. Wilson and B. C. Allibone, J. Inst. Petroleum Tech. **11**, 180 (1925).
[4] A. J. Spilker, Zeits. f. angew. Chemie **39**, 997 (1926).
[5] G. Hugel, Chemie et Ind. **26**, 1282 (1932).
[6] L. A. Mikeska, Ind. Eng. Chem. **28**, 970 (1936).
[7] W. Kauzmann and H. Eyring, J. Am. Chem. Soc. **62**, 3113 (1940).
[8] S. Arrhenius, Medd. Vetensk. Nobel. **3** [20] (1916).
* Recently R. M. Barrer, Trans. Faraday Soc. **39**, 48 (1943) has considered this type of equation.

TABLE I.

No.	Name and formula	$A \times 10^{-3}$	$E \times 10^{-3}$	Reference
1.	*n*-Pentane, C_5H_{12}	5.520	1.504	*a*
2.	*n*-Hexane, C_6H_{14}	5.598	1.690	*a*
3.	*n*-Heptane, C_7H_{16}	5.842	1.858	*a*
4.	*n*-Octane, C_8H_{18}	6.641	2.088	*a*
5.	*n*-Nonane, C_9H_{20}	8.485	2.394	*b*
6.	*n*-Decane, $C_{10}H_{22}$	8.936	2.565	*b*
7.	*n*-Undecane, $C_{11}H_{24}$	9.940	2.778	*b*
8.	*n*-Dodecane, $C_{12}H_{26}$	11.51	3.010	*b*
9.	*n*-Tetradecane, $C_{14}H_{30}$	11.40	3.203	*c*
10.	*n*-Hexadecane, $C_{16}H_{34}$	16.12	3.652	*c*
11.	*n*-Octodecane, $C_{18}H_{36}$	18.40	3.891	*c*
12.	*n*-Dotriacontane, $C_{32}H_{66}$	18.66	4.922	*c*
13.	Benzene, C_6H_6	9.803	2.428	*a*
14.	Toluene, $C_6H_5—CH_3$	5.777	2.059	*a*
15.	Ethyl-benzene, $C_6H_5CH_2CH_2$	5.336	2.084	*a*
16.	*n*-Butyl-benzene, $C_6H_5C_4H_9$	3.139	2.033	*d*
17.	2-Methyl-butane, C—C(—C)—C—C*	6.099	1.549	*a*
18.	2-Methyl-2-butene, C—C(—C) : C—C	4.811	1.375	*a*
19.	2-Methyl-1,3-butadiene (Isoprene), C : C(—C)—C : C	5.382	1.434	*a*
20.	1,5-Hexadiene, C : C—C—C—C : C	5.823	1.628	*a*
21.	2-Methyl-pentane, C—C(—C)—C—C—C	5.818	1.676	*a*
22.	3-Methyl-pentane, C—C—C(—C)—C—C	5.194	1.638	*e*
23.	2,2-Dimethyl-butane, C—C(—C)(—C)—C—C	8.002	1.978	
24.	2,3-Dimethyl-butane, C—C(—C)—C(—C)—C	8.563	2.035	*e*
25.	2,3-Dimethyl-1,3-butadiene, C : C(—C)—C(—C) : C	7.054	1.724	*e*
26.	2-Methyl-hexane, C—C(—C)—C—C—C—C	9.122	2.070	*a*
27.	4,4-Dimethyl-1-pentene, C : C—C(—C)(—C)—C	9.057	2.194	*f*
28.	2,5-Dimethyl-hexane, C—C(—C)—C—C(—C)—C	6.142	1.974	*e*
29.	2,7-Dimethyl-octane, C—C(—C)—C—C—C—C—C(—C)—C	7.113	2.382	*e*

TABLE I.—*Continued.*

No.	Name and formula	$A \times 10^{-3}$	$E \times 10^{-3}$	Reference
30.	Cyclopentane, 	5.554	1.878	*e*
31.	Methyl-cyclopentane, 	6.603	2.055	*e*
32.	Cyclohexane,	15.21	2.905	*e* and *a*
33.	Methyl-cyclohexane, 	2.352	1.678	*f* and *d*
34.	1,2-Dimethyl-cyclohexane, 	17.98	3.074	*f*
35.	1,3-Dimethyl-cyclohexane, 	8.150	2.353	*f*
37.	1,4-Dimethyl-cyclohexane, 	14.89	2.861	*f*
38.	1,2-dimethyl-benzene, *o*-$C_6H_4(CH_3)_2$	6.141	2.277	*a*
39.	1-cyclohexyl-2-methyl-propane, 	8.787	2.722	*d*
40.	Triphenyl-methane, $(C_6H_5)_3CH$	15.38	4.600	*d*
41.	Biphenyl, $C_6H_5—C_6H_5$	32.07	4.226	*d*
42.	Decahydro-naphthalene, 	7.252	3.034	*d*
43.	1,2,3,4-tetrahydro-naphthalene, 	9.800	3.112	*d*
44.	Naphthalene, $C_{10}H_8$	580.3	5.977	*d*

* Hydrogen atoms are omitted. C—C indicates a single bond, C : C a double bond.

[a] Landolt-Börnstein, *Tabellen*, main volume, Part I, pp. 130, 149–52.
[b] Bingham and Fornwalt, J. Rheol. 1, 372 (1930).
[c] Landolt-Börnstein, *Tabellen*, third supplement, p. 162.
[d] Landolt-Börnstein, *Tabellen*, second supplement, pp. 100–105.
[e] *International Critical Tables*, Vol. VII, pp. 216–18.
[f] Landolt-Börnstein, *Tabellen*, first supplement, p. 134.

and may safely be attributed to errors in a particular viscosity measurement. The usual difference is about 0.005 (1 percent). It should be noted that, while viscosities can be measured very accurately, the temperature is often not reported accurately, particularly in high temperature measurements, and this gives rise to large deviations from calculated values. In view of these considerations it may safely be said that the Arrhenius equation holds to a fair degree of accuracy, and the deviations may be attributed to variation of λ_1, λ, $\Delta S^{\neq}$, and $\Delta H^{\neq}$ with temperature.

EFFECT OF VARIOUS STRUCTURAL FEATURES

By comparing groups of compounds which differ in only one structural feature, we can determine how this feature affects A and E. Since A is very sensitive to errors in E, comparison of the A values cannot be put on a quantitative basis, but qualitative trends can be observed. Since the E values are more accurate, greater confidence can be placed in our conclusions concerning them.

The results may be summarized as follows:

1. Addition of a methylene group to a molecule increases E by about 200 calories and A by about 1000 poise^{-1}.

2. A and E are both increased greatly by branching the carbon chain. Since branching causes a smaller increase in E for an equal change of A than does lengthening the chain, a highly branched hydrocarbon of low molecular weight should have a smaller temperature coefficient than a straight-chain compound of sufficiently high molecular weight to have the same A value.

3. Branching seems to have a greater effect on compounds which are already branched than on normal hydrocarbons.

4. The position of a side chain has very little effect on A and E. More data will be necessary before we will be able to say which arrangements tend to have higher values for these constants.

5. A is a linear function of chain length, while ΔE becomes a little smaller with increasing chain length, as is shown in Fig. 1. A redetermination of the viscosity for $n-C_{30}H_{64}$ would be of great significance.

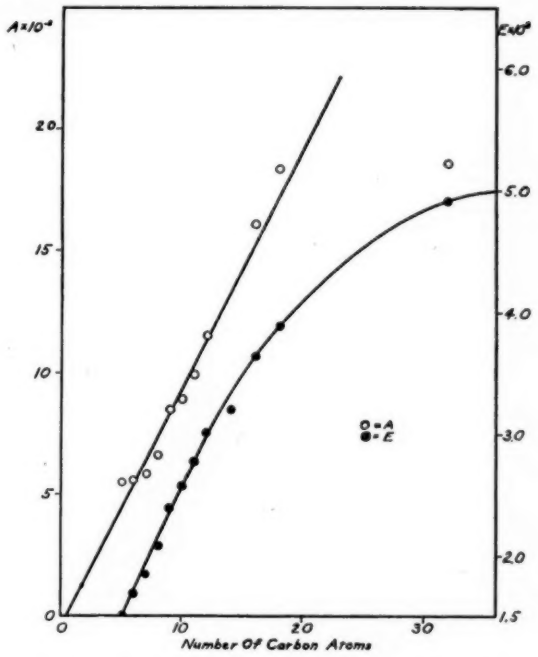


FIG. 1. Variation of A and E with chain length.

6. Unsaturation seems to decrease A and E, but more data are necessary before the effect of various kinds of unsaturated bonds can be determined quantitatively.

7. Cyclic compounds have much larger values of A and E than the corresponding aliphatic compounds. In the formation of a five-membered ring A is increased by about 500 poise^{-1} and E by about 380 calories. In the formation of six-membered rings, A is increased by about 10,000 poise^{-1} and E by about one kilocalorie.

8. Reduction of an aromatic ring to an alicyclic increases A by about 9000 poise^{-1} and E by about 700 calories.

9. A and E seem to be very much larger for condensed ring systems than for single rings, but the data on these compounds are not very consistent nor complete.

We wish to thank Professor Eyring for his helpful discussions.

A Direct Experimental Determination of the Electron Affinity of Oxygen*

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The electron affinity of oxygen atoms for one electron, the negative of the energy change at absolute zero of the reaction

$$e^- + O_{gas} \rightarrow O^-_{gas},$$

has been determined to be 70.8±2.0 kcal./mole. The method used was to determine the ratio of negative ions to electrons leaving a hot filament surface exposed to oxygen gas at a low pressure.

GENERAL

IT is possible to determine experimentally the electron affinity of an atom, i.e., the negative of the energy change at absolute zero accompanying the reaction

$$X_{gas} + e^-_{gas} = X^-_{gas},$$

provided that the number of gas atoms and the ratio of electrons and ions leaving a surface of known temperature can be determined, provided that the accommodation coefficient is unity, and provided that information is available for the calculation of the standard free energy of each species at unit pressure and the experimental temperature. This method has already been successfully employed in the determination of the electron affinity of chlorine[1,2] and iodine.[3] The method is extended here to the investigation of the electron affinity of oxygen for a single electron, corresponding to the reaction at absolute zero

$$O_{gas} + e^-_{gas} = O^-_{gas}. \quad (1)$$

Measurements were made using oxygen gas as a carrier over a range of temperatures from 2030°K to 2230°K, of pressures of oxygen from 0.1 micron to 2 microns of mercury, and over a 20-fold range in electron current. An average value of 70.8±2.0 kcal./mole was obtained, which value evidenced—within the limits of experimental error—no trend with temperature, pressure, or electron current.

The method of calculation of the electron affinity of oxygen is similar to that used by McCallum and Mayer for chlorine[1] with the exception that the assumption of complete dissociation of the molecule cannot be made in this case, the percent dissociation ranging from 29 to 90. Instead, one obtains the expression

$$-\Delta E_0^0 = RT_s \ln \left[\frac{I_i}{I_e P_O} \left(\frac{m_i}{m_e} \right)^{\frac{1}{2}} \times \left(\frac{2\pi m_e k T_s}{h^2} \right)^{\frac{3}{2}} \frac{2kT_s}{a} \frac{Q_{iO}}{Q_{iO^-}} \right], \quad (2)$$

where $-\Delta E_0^0$ is the electron affinity of oxygen; I_i/I_e is the experimental ratio of ion and electron currents; m_i and m_e are the masses of the oxygen ion and electron, respectively; T_s is the temperature of the filament; a is the value of an atmosphere pressure expressed in dynes/sq. cm; Q_{iO} and Q_{iO^-} are the internal partition functions of the oxygen atom and ion, respectively; and R, k, and h have their usual significance. The quantity P_O is the pressure of a hypothetical oxygen atom gas at the temperature of the filament for which the number of atoms hitting the filament would be equal to the number leaving under the conditions of the experiment. This pressure is to be calculated from the observed pressure of oxygen gas surrounding the filament and the dissociation constant of oxygen.

The exact numerical value of the internal partition function for the oxygen ion is not known with certainty since its spectrum has not been observed experimentally. However, an approximate value may be obtained from the

*Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

† Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Columbia University.

[1] Kenneth J. McCallum and Joseph E. Mayer, J. Chem. Phys. **11**, 56 (1943).

[2] J. J. Mitchell and Joseph E. Mayer, J. Chem. Phys. **8**, 282 (1940).

[3] P. P. Sutton and Joseph E. Mayer, J. Chem. Phys. **3**, 20 (1935).

following considerations. Since the electron configuration of the oxygen ion is similar to that of the fluorine atom, the ground state is ^2P, the low lying term being the $^2P_{3/2}$ with the next higher, $^2P_{1/2}$, separated from it by less than the separation of these two terms in the fluorine atom or 407.0 cm^{-1}. Moreover, extrapolation of the curve obtained by plotting the log of the separation in wave numbers of the $^2P_{3/2}$ and the $^2P_{1/2}$ terms as a function of the log of $Z-2$, where Z is the nuclear charge of the ion, of the isoelectronic sequence Al V, Mg IV, Na III, Ne II, and F I indicates that the separation of these terms for the O^- ion is less than 190 cm^{-1} (see Fig. 1). Higher terms do not contribute at the experimental temperatures. Q_{iO} lies, therefore, between $4+2e^{-273/T_s}$ and 6, and it can be assumed that

$$Q_{iO^-}=6.0, \tag{3}$$

without causing an appreciable error in the calculation, since the temperature T_s is about 2000°K.

The ground level of the neutral oxygen atom is an inverted ^3P, consisting of the $^3P_2$, $^3P_1$, and $^3P_0$ terms. There are no other low lying levels with the higher $^1D_2$ and $^1S_0$ terms lying high enough to be neglected. The internal partition function of the neutral oxygen atom is

$$Q_{iO}=5+3e^{-226.2/T_s}+e^{-324.5/T_s}.$$

The log of this quantity, between 2000°K and 2400°K, may be approximated by

$$\log Q_{iO}=0.9124+0.09342\times10^{-4}T_s. \tag{4}$$

Substituting the above expressions for Q_{iO^-} and Q_{iO} in (2), the resulting equation for $-\Delta E_O^0$, in kcal./mole, may be written

$$-\Delta E_O^0=(4.574T_s/1000)\,(\log \Delta_i\times10^4/\Delta_e - \log P_O+9.963\times10^{-4}T_s - 1.121\times10^{-7}T_s^2+4.793), \tag{5}$$

in which Δ_i/Δ_e is the ratio of the galvanometer deflections due to ions and electrons, respectively; P_O is the pressure of oxygen atoms in microns, and T_s is the experimental filament temperature.

The calculation of log P_O from the observed pressure of oxygen molecules may be accomplished by the following method. The sum of the number of oxygen molecules leaving the filament plus one-half the number of oxygen atoms leaving the filament is equal to the number of oxygen molecules striking. The number Z of particles of mass m striking a unit area of surface in unit time is related to the pressure and temperature by the equation $Z=P/(2\pi mkT)^{\frac{1}{2}}$. Substituting this expression for each species in the material balance above yields the following equation for the pressure of a hypothetical atomic oxygen gas at the temperature of the filament, from which as many atoms would hit the filament as are leaving it under the conditions of this experiment:

$$P_O=2^{-\frac{1}{2}}K_D\{[1+8P/K_D(T_s/T_r)^{\frac{1}{2}}]^{\frac{1}{2}}-1\}. \tag{6}$$

In this K_D is the dissociation constant for the reaction $O_2=2O$, T_r is the temperature of the molecular oxygen gas striking the filament (room temperature), T_s is the temperature of the gases leaving the filament (filament temperature), P is the observed pressure of O_2 gas in atmospheres, and P_O is the pressure of atoms in atmospheres.

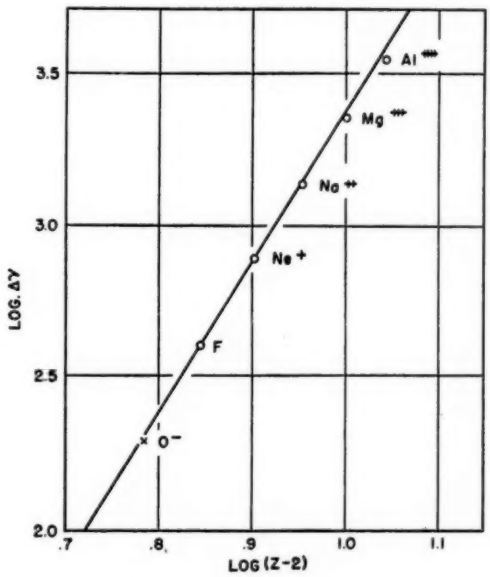

FIG. 1. Plot of log $\Delta\gamma 2p_{\frac{1}{2}}-2p_{\frac{3}{2}}$ *vs.* log $(Z-2)$.

The assumption is made in this that the accommodation coefficient of the oxygen molecules hitting the surface is unity, i.e., that the relative numbers of atoms and molecules leaving the surface is the same as if the filament were sur-

rounded by a gas at filament temperature. In support of this assumption we may point out that experiments of Bryce[4] have shown that the dissociation of H_2 on a tungsten filament follows the simple equilibrium hypothesis. This has been shown by calculations of Doty[5] based on Bryce's data.

It is interesting to note at this juncture that an investigation of the history of the oxygen atoms after leaving the hot filament indicated

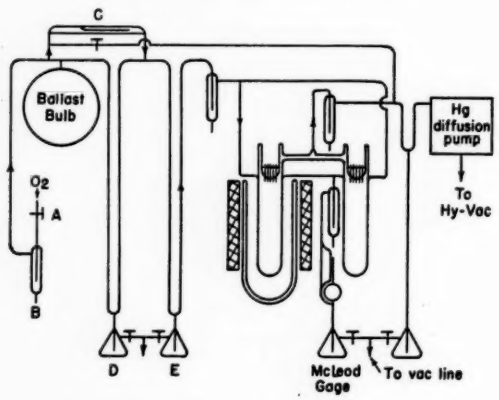

FIG. 2. Schematic diagram of apparatus.

that they did not persist as atoms and neither reacted with nor were absorbed by the metal parts or walls, but instead recombined to form oxygen molecules. The percent recombination was found to be 100 ± 10.

Returning to the calculation of P_O, the dissociation constant K_D can be calculated in the usual fashion from statistical mechanics, employing the necessary spectroscopic data of atomic and molecular oxygen. The resulting expression for K_O contains several exponentials, and can be greatly simplified by taking the log of this expression and expanding by Taylor and McLaurin series about the temperature $T_0=2200°K$. The resulting equation for $\log K_D$, which may be used from 1980°K to 2420°K, is

$$\log K_D=-25{,}617/T+5.8720+4.4450\times10^{-4}T-0.5669\times10^{-7}T^2. \quad (7)$$

EXPERIMENTAL

The apparatus used in the determination of the electron affinity of oxygen is shown diagrammatically in Fig. 2. Electrolytic tank oxygen of better than 99.5 percent purity, obtained from the Ohio Chemical and Manufacturing Company, was slowly introduced at A and then purified by passing it through a liquid nitrogen trap B as a precautionary measure to remove water and the halogens, the only substances likely to cause an appreciable error in the determination of the electron affinity of oxygen. The mercury in the cut-off D was raised and the pressure in the 2-liter ballast bulb and behind the capillary leak C was allowed to rise to such a value as to give the desired pressure in the experimental and control tubes, after which the oxygen supply was cut off by closing stopcock A. In this way a constant pressure was maintained behind the leak, the amount of gas passing through the capillary having a negligible effect on the pressure in the ballast bulb. After passing through the experimental and control tubes, which were in parallel, the oxygen flowed through a Princeton model diffusion pump with suitable backing. With this arrangement of introduction and pumping of gas, it was possible to provide a constant flow through the tubes (amounting, under operating conditions, to about 1300 cc/sec.) at any pressure between 0.001 and 100 microns of mercury.

The construction of the experimental tube and the experimental procedure used for the measurement of the ion and electron currents were essentially the same as those described in a previous paper.[1] The tube contained a cylindrical plate, between similar guard rings, and a radially shaped grid, all being coaxial with a tungsten filament. Ions and electrons leaving the filament were accelerated to the plate by a positive potential, whereas the electrons could be deflected to the grid by a magnetic field induced by a solenoid coaxial with the filament.

A more accurate means for obtaining the voltage across the filament than that described in reference 1 was used, the detailed construction of which is shown in Fig. 3. The upper and lower filament supports were welded to tungsten through glass leads and were constructed of General Electric tungsten wire with a diameter that was $(18)^{\frac{1}{2}}$ times that of the tungsten filament. (With this ratio of diameters, within the precision of the temperature measurements, the voltage correction for the cooling effect of the leads could be simplified by assuming that the temperature at the ends of the filament was one-quarter of the maximum temperature.[6]) The lower support consisted of a bifilial coaxial spring and was provided in order to keep the filament taut and centered within the radially shaped grid.

The filament current passed through one lead of each of the bottom and top supports while the remaining leads of the two supports were used to measure the potential across the filament. The filament itself was a 10-cm General Electric tungsten wire with a diameter of 0.02 cm and was spot-welded to the upper and lower supports. The spot welding caused little distortion of either the filament or supports at the points of contact. With this arrangement, the voltage across the filament could be measured directly. In addition, the error in the voltage due to thermal po-

[4] G. Bryce, Proc. Camb. Phil. Soc. **32**, 648 (1936).
[5] Paul M. Doty, J. Chem. Phys. **11**, 557 (1943).
[6] H. Jones and I. Langmuir, Gen. Elec. Rev. **30**, 310 (1927).

tentials was found to be less than 0.2 percent at 2000°K, as determined by reversing the current through the filament and again measuring the potential drop. This latter procedure was carried out in the measurement of all temperatures and was particularly significant in the measurement of the cold resistance of the filament.

In order to examine carefully the temperatures of the filament in a vacuum in the experimental tube as calculated from the five commonly used functions of current and voltage,[6] a control tube was put in the gas flow line in parallel with the experimental tube. It consisted simply of a filament, taken from the same piece of stock wire from which the filament in the experimental tube was taken, with similar supports and in a tube of approximately the same size. The filament of this tube was connected in series with that in the experimental tube so that the current in each filament would be the same. During a run in vacuum, the voltage across each filament and the current were measured, and these data were combined with the individual filament dimensions in order to calculate and compare the temperatures of each. It was found that for a given filament the temperatures as calculated from all five functions agreed to within 10 to 20°C in both the experimental and control tubes, with the disagreement of the temperatures of both filaments as calculated from the same function being even less than 10°C.

The resistance function was used to calculate the filament temperature when runs were made in oxygen, since other functions give erroneous values in the presence of gas. Nevertheless, it is to be noted that calculation of the temperature by means of the other functions gave values which did not differ from the resistance temperature by more than thirty degrees, with the agreement in nearly all the cases being better than 20°C. Calculation of the temperature difference to be expected under the experimental conditions used indicates that one should not observe a difference greater than 10°C.

The cause for the discrepancy found in temperatures calculated from the various functions was due primarily to the fact that it was necessary to determine the diameter of a filament from the measurement of the cold resistance before and after a run, a method which is less accurate than the usual method of weighing and measuring the length of the filament to calculate the diameter. It was necessary to employ this less accurate method since the filaments were attacked by oxygen, about five percent of the molecules striking a given filament reacting to form tungsten oxides and thus decreasing the diameter. For this reason, it was also necessary to limit the time of a run to about twenty minutes.

The ion currents encountered in this work gave galvanometer deflections of about 3 cm which were constant to about 5 percent. This precision was attained by surrounding the experimental tube by a Dewar of liquid nitrogen, which reduced the fluctuations in both the ion and electron currents. This was presumably due to the removal of condensible gases given off by the filament and grid. There was no other apparent source of condensible gases, including mercury, since the tubes were protected from these by liquid nitrogen traps on the oxygen inlet and exit tubes and on the tube to the McLeod gauge used in measuring oxygen pressures.

With these low ion currents it was important to eliminate the possibility that part of the ion current might possibly be due to electrons, resulting from their incomplete removal by the grid. The completeness of removal of electrons by the grid was checked in two ways. First it was found that varying the current in the solenoid from about 4 to 7 amperes had no effect on the ion current, the ion current remaining constant. In addition, the oxygen supply was quickly cut off after a reading by raising the mercury in cut-off E (Fig. 2), and in every case, the ion current dropped to zero.

DISCUSSION OF RESULTS

In Table I are tabulated the results of sixteen experimental determinations of the electron affinity of oxygen as calculated from the individual sets of data, employing Eqs. (5), (6), and (7). The percent error for each value is also indicated and was calculated from the estimated precision of the individual measurements of temperature, pressure, electron current, and the ion current in each set of data. The error in temperature was from 2–4 percent; in pressure,

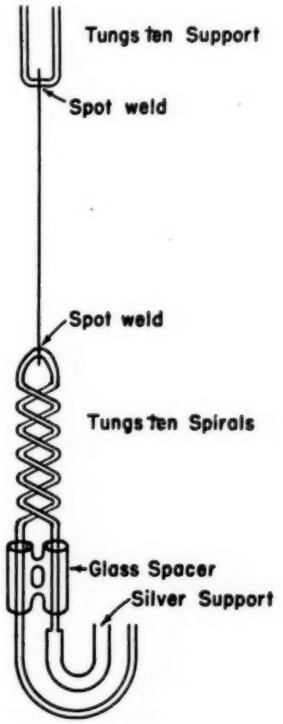

FIG. 3. Filament supports.

TABLE I.

No.	T, °K	$P_{\text{microns } O_2}$	% dissoc.	K_D $O_2=2O$	$O+e=O^-$ $-\Delta E_O^0$ kcal./mole	Estimated total Max. % error	Weight	$O_2+e=O_2^-$ $-\Delta E_{O_2}^0$ kcal./mole
1	2150	0.067	81	4.71×10^{-6}	75.62	9.5	1	83.27
2	2230	0.37	85	1.35×10^{-5}	72.18	6.0	1	81.11
3	2090	0.50	53	2.00×10^{-6}	72.63	6.0	1	74.46
4	2230	2.0	59	1.24×10^{-5}	68.92	5.2	2	72.04
5	2230	2.0	59	1.24×10^{-5}	68.37	5.1	2	70.49
6	2230	1.6	63	1.24×10^{-5}	65.81	5.5	2	69.67
7	2090	1.10	40	1.97×10^{-6}	70.33	2.7	3	70.01
8	2110	0.86	48	2.61×10^{-6}	70.51	2.8	3	71.57
9	2220	0.50	79	1.10×10^{-5}	69.76	3.9	3	77.11
10	2220	0.50	79	1.10×10^{-5}	71.05	3.6	3	78.40
11	2180	1.15	58	6.62×10^{-6}	69.88	3.8	3	72.72
12	2180	1.07	59	6.62×10^{-6}	69.82	3.9	3	72.87
13	2030	1.00	29	8.34×10^{-7}	73.59	2.1	3	71.41
14	2170	0.094	90	5.10×10^{-6}	66.47	8.9	1	77.07
15	2170	0.129	87	5.10×10^{-6}	64.66	9.9	1	74.34
16	2170	0.129	87	5.10×10^{-6}	65.43	9.2	1	75.10
				Average value	70.8			73.8

10–50 percent; and in ion-electron current ratio, 12–44 percent; resulting in a 1–3 percent, a 0.5–4 percent, and a 1–4 percent maximum error, respectively, in the calculated value of the electron affinity. The average value of the electron affinity was calculated by weighting each value inversely to the square of the percent error in the customary fashion. The average value calculated in this way was 70.8 kcal./mole with a standard deviation of 0.8 kcal./mole.

The authors do not believe that the experimental certainty is as great as the formally calculated error of 0.8 kcal./mole would indicate. The tacit assumption of a zero reflection coefficient may not be strictly true and cannot be corrected for since there are no experimental data that indicate the actual value of the reflection coefficient of oxygen and similar molecules. The assumption of a reflection coefficient greater than zero would increase the calculated electron affinity. In view of these considerations, it is not unreasonable to assume a larger probable error of 2.0 kcal./mole in the average value of $-\Delta E_O^0$.

Since the calculated election affinity should be independent of the conditions, such as temperature, pressure, percent dissociation of oxygen molecules, or electron emission, in the reaction vessel, a plot of the values of $-\Delta E_O^0$ obtained in Table I as a function of these variables should result in a horizontal line. In Fig. 4 are shown the results of some of these plots. Similar plots of $-\Delta E_O^0$ as a function of the calculated value of the equilibrium pressure of oxygen atoms or the electron emission yielded curves similar to that against P_{O_2}. These curves are only approximate since they were obtained by the method of least squares with an arbitrary assignment of weights of 1, 2, or 3 to the individual points, a more precise weighting being unwarranted. The curves indicate that there is slight, if any, trend of the obtained electron affinity with temperature, pressure, electron emission, or percent dissociation.

Several values of the electron affinity of oxygen have been obtained by other methods. The empirical extension of ionization potentials of the appropriate isoelectronic series yielded a value of 88 kcal./mole.[7] Similar calculations have also yielded the values 23,[8] 50,[9] and 36[10] kcal./mole. A direct experimental determination of the electron affinity of oxygen has been made by Lozier and by Hanson by the analysis of negative ion currents produced by collision of low energy electrons with oxygen,[11] carbon mon-

[7] G. Glockler, Phys. Rev. **46**, 111 (1934).
[8] R. Bacher and S. Goudsmit, Phys. Rev. **59**, 948 (1934).
[9] J. Mayer and M. Maltbie, Zeits. f. Physik **75**, 748 (1932).
[10] Hellmann and M. Mamotenko, Acta Physicochimica **7**, 141 (1937).
[11] W. Lozier, Phys. Rev. **46**, 268 (1934).

oxide,[11] and nitric oxide.[12] The values of 51±5 and 46±9 kcal./mole, respectively, were obtained.

The reason for the disagreement between the values obtained by the method of Lozier and that obtained by this method is not apparent. There exists the possibility that the ions leaving the hot filament, under the experimental conditions used here, consisted of oxygen molecule ions instead of atomic oxygen ions. However, this seems unlikely since the electron affinity of molecular oxygen has been determined experimentally by two different methods and has yielded the values 3 kcal./mole[13] and 8 kcal./mole.[14] On the other hand, the electron affinity of molecular oxygen has been estimated from cycles involving the heat of dissociation and heat of solution of HO_2,[15] leading to a value of 62 kcal./mole.

It is to be noted at this point that the possibility of the formation of O^- is excluded since the total electron affinity of oxygen corresponding to the reaction $O+2e=O^-$ has been calculated to be negative by 225 kcal./mole.[16]

Assuming that the ions observed were O_2^- resulting from the reaction

$$O_2+e=O_2^-,$$

calculation of the corresponding electron affinity for each set of data in Table I, yielded the values given in the final column of Table I. The equation used in calculating these values was derived by the same method used to obtain Eq. (5), resulting in the following expression for the electron affinity of molecular oxygen:

$$-\Delta E_O{}^0=4.574T_e/1000[\log.(I_i\times10^4/I_e) -\log P_{O_2}\text{ (observed)}+7.896\times10^{-4}T_e -0.897\times10^{-7}T_e{}^2+4.704].$$

It was assumed in this derivation that the partition functions of O_2 and O_2^- have approximately the same value, which is probably not in error by more than 2 kcal./mole.

If the electron affinity which was being measured in this experiment was essentially that of O_2, then the calculated value should be independent of the tube conditions. That such was not the case is evidenced by the fact that the electron affinity is seen to be markedly dependent on the pressure of oxygen. The average value obtained of 74 kcal./mole marks an upper limit to the electron affinity of O_2.

In conclusion, it is to be noted that probably the main source of error is in the assumption of a zero reflection coefficient, but that the effect of a reflection coefficient different from zero would

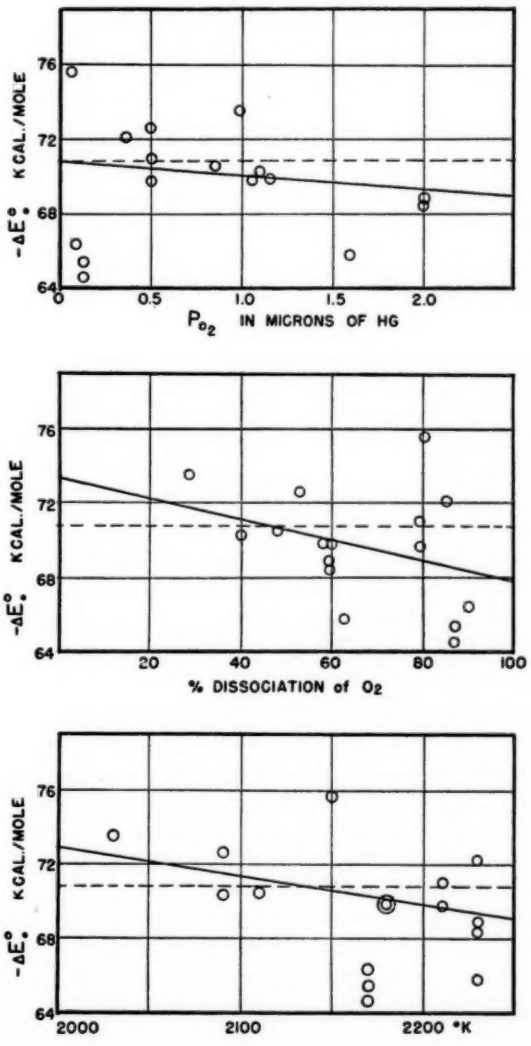

FIG. 4. $-\Delta E_O{}^0$ *vs.* observed pressure, percent dissociation, and temperature for $0+e=0^-$.

[12] G. Hanson, Phys. Rev. **48**, 476 (1935).
[13] N. E. Bradbury, J. Chem. Phys. **2**, 827 (1934); *ibid.* **2**, 835 (1934).
[14] L. B. Loeb, Phys. Rev. **48**, 684 (1935).
[15] J. Weiss, Trans. Faraday Soc. **31**, 966 (1935).
[16] F. R. Bichowsky and F. Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Company, New York, 1936).

be to increase still further the value obtained, resulting in even a wider discrepancy with the experimental value of Lozier's. Also, it has been pointed out above that impurities, particularly water, can play no role since the tube was adequately protected by liquid nitrogen traps. The formation of possible pathological molecule ions such as WO_2^- or WO_3^- having electron affinities comparable with that of atomic oxygen is not excluded, but is inherently unlikely.

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The Resonance Emission of Cadmium Hydride Bands in Cadmium Photosensitized Reactions of Hydrocarbons*

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(Received November 13, 1943)

An investigation has been made of the resonance excitation of cadmium hydride bands in mixtures of ethylene or propane with cadmium vapor illuminated with λλ3261 and 2288. With λ3261 no resonance excitation with ethylene could be detected. With propane, CdH bands were emitted with fair intensity, thus proving that the primary process in the cadmium photosensitized reactions of the paraffins is

$$Cd(5^3P_1)+RH\rightarrow CdH+R.$$

With λ2288 no resonance emission could be detected, but the results were inconclusive.

INTRODUCTION

IN recent years we have investigated a series of reactions of hydrocarbons photosensitized by cadmium, the two resonance lines, λ3261 and λ2288, being employed.[1] With λ3261 and the paraffins, the quantum yield is of the order of 0.2 to 0.6, and the evidence points strongly to a C−H bond split as the initial step. On energetic grounds this can only occur if the primary process involves the formation of CdH, i.e.,

$$Cd(5^3P_1)+RH\rightarrow CdH+R, \quad (1)$$

followed by

$$CdH\rightarrow Cd(5^1S_0)+H. \quad (2)$$

With λ3261 and olefins the quantum yield is very small, about 0.01, and it appears to be established that this is due to the quenching process involving the double bond. What little reaction does occur might be due to CdH formation by (1), or might involve a pseudo-thermal polymerization or some other mechanism.

With λ2288, reaction occurs readily with both olefins and paraffins. In this case the excitation energy is greater than the C−H bond strength, and it is thus possible for a C−H bond split to occur directly, without the intermediate formation of cadmium hydride.

Bender[2] and Olsen[3] have observed resonance excitation of the cadmium hydride bands in the neighborhood of λλ4791, 4571, 4500, 4310, etc., when a mixture of cadmium vapor and hydrogen is illuminated with light from a cadmium-hydrogen discharge, thus proving the formation of CdH by the process

$$Cd(5^3P_1)+H_2\rightarrow CdH+H.$$

It seemed of interest to carry out a similar investigation with hydrocarbons as a check on the mechanisms proposed for cadmium photosensitized reactions.

* Contribution No. 1174 from The National Research Laboratories, Ottawa, Canada.

[1] See, for example, E. W. R. Steacie and R. Potvin, J. Chem. Phys. **7**, 782 (1939). E. W. R. Steacie, D.J. LeRoy, and R. Potvin, J. Chem. Phys. **9**, 306 (1941). E. W. R. Steacie and D. J. LeRoy, J. Chem. Phys. **10**, 22 (1942); *ibid.* **11**, 164 (1943). D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. **10**, 683 (1942).

[2] P. Bender, Phys. Rev. **36**, 1543 (1930).

[3] L. O. Olsen, J. Chem. Phys. **6**, 307 (1938).

EXPERIMENTAL

The experimental method was essentially that employed by Bender and by Olsen. Radiation from a cadmium-hydrogen discharge entered a cell containing cadmium vapor and a hydrocarbon or other gas. If cadmium hydride was present in the cell, CdH bands were emitted as fluorescence.

A quartz cadmium-hydrogen discharge tube was used, similar to that of Ellett.[4] The tube was in the form of a spiral, and made $3\frac{1}{2}$ turns around the resonance cell. It was operated at about 2.5 kva. It was found difficult to obtain reproducible results with Ellett's arrangement in which the metal vapor diffused into the hydrogen stream from a side-tube. The arrangement was therefore modified so that hydrogen flowing into the discharge passed through a quartz tube heated to about 300°C and containing a 1 : 1 cadmium-tin alloy. This gave more reproducible saturation of the gas with cadmium vapor. The connecting tubing between the saturator and the discharge tube was wound with Nichrome ribbon and kept at about 350°C.

The resonance cell was of the usual type with a plane window on one end and a light trap at the other. It was blackened except for part of the end window and the section opposite the discharge tube. It was found that a very convenient, adherent, flat black paint for optical purposes at temperatures up to 300°C can be made by grinding together lamp black and "Shellkote," a high temperature lacquer. For experiments with λ3261 the resonance cell was made of Pyrex glass, while for λ2288 fused quartz was used. The resonance cell and the central portion of the discharge tube were contained in an electric furnace, the heaters of which were arranged so as to make sure that the window of the cell was slightly hotter than the rest of the furnace.

Since the purpose of the work was to investigate gases which underwent photosensitized decomposition, it was essential that means be taken to prevent effects due to the products of the photolysis. This was especially important in the case of propane, since hydrogen is one of the products, and this leads readily to resonance emission of the CdH bands. Trial experiments with propane showed that sufficient decomposition occurred during the shortest feasible exposure to vitiate the results. A flow system was therefore used in which the contact time was small. The gas under investigation entered the system through a calibrated capillary, passed through a saturator containing a cadmium-tin alloy similar to that described above, entered the resonance cell near the front window, passed through the cell, and then on to the pump.

The spectrograph used was a Hilger intermediate quartz spectrograph with a dispersion of about 75A per mm at 4500A. This was ample, since all that was required was the detection of the main cadmium hydride bands. Eastman 40 plates were used for experiments with λ3261, and U.V. sensitized plates for work with λ2288.

Results with λ3261

With the flow system used it was not possible to obtain a reproducible supply of cadmium vapor when the system was evacuated, since the cell was open and the vapor distilled to the colder parts of the apparatus. It was therefore not practical to compare the fluorescence with the cell evacuated with that in the presence of a foreign gas. Instead a stream of nitrogen was used for comparison purposes, since its quenching efficiency is very small.[5]

Nitrogen

With nitrogen flowing through the system at pressures from 0.5 to 25 mm an intense green fluorescence was visible. With exposures of from 10 to 60 seconds, photographs showed a very intense emission of the resonance line at 3261A, together with the main lines of the secondary spectrum, λλ5086, 4800, 4678, 3611–14, 3466–68, and 3404. With long exposures the cadmium hydride bands were faintly visible at 4500 and 4310A owing to scattered light.

Hydrogen

In the presence of hydrogen, in agreement with previous work, the whole cadmium spectrum was quenched, the visible green fluorescence disappeared, and cadmium hydride bands at 4310,

[4] A. Ellett, J. Opt. Soc. Am. **10**, 427 (1925).

[5] H. C. Lipson and A. C. G. Mitchell, Phys. Rev. **48**, 625 (1935).

4500, and 4571A were emitted with high intensity. The optimum hydrogen pressure for the excitation of the bands was about 0.5 mm. With longer exposures bands at 4791, 4835, and 4198A were also evident.

Ethylene

With ethylene at pressures from 0.5 to 7 mm, λ3261 and the secondary spectrum were strongly quenched as would be expected from the high quenching cross section of ethylene for λ3261.[6] No detectable emission of the CdH bands occurred, however. In view of the very low quantum yield of the cadmium photosensitized reactions of ethylene, this is what would be expected, since a large formation of CdH would almost certainly be accompanied by a high quantum yield. The very small amount of reaction which does occur with ethylene may or may not involve the formation of CdH in the primary step, since the present method could hardly be expected to detect such a small concentration of cadmium hydride.

Propane

With propane at pressures above 1 mm appreciable quenching occurred, and CdH bands were emitted in fair intensity. The optimum pressure for the excitation of the bands was about 7 mm. Under optimum conditions the intensity of the bands was of the order of $\frac{1}{8}$ that with hydrogen at 0.5 mm. In view, however, of the relatively small quenching by propane, which necessitated the use of much higher pressures, it is not possible to make any quantitative comparison of the relative efficiencies of band excitation by hydrogen and propane. The results do indicate, however, that the excitation of the bands in the presence of propane is quite efficient, and prove definitely that at least a major portion of the quenching of λ3261 by propane occurs by the mechanism

$$Cd(5^3P_1)+C_3H_8\rightarrow CdH+C_3H_7.$$

This furnishes complete confirmation of the assumptions which we have made previously regarding the mechanism of the cadmium photosensitized reactions of the paraffins.

Results with λ2288

Experiments with λ2288 were made with a quartz resonance cell. No attempt was made to filter out λ3261, but instead results obtained with λ3261 and λ2288 together were compared with those obtained with λ3261 alone. Under conditions similar to those described in the preceding section, there was no detectable excitation of cadmium hydride bands by λ2288 in the presence of either ethylene or propane. The result is rather inconclusive, however, since (a) λ2288 was considerably weaker than λ3261, (b) scattered light was somewhat more troublesome, (c) owing to the short lifetime of the 5^1P_1 state, quenching of λ2288 by foreign gases is relatively small, and (d) the high absorption coefficient of cadmium vapor for λ2288 would result in a large fraction of the incident radiation being absorbed near the wall, and wall deactivation, etc., might become important. It is thus not possible to decide whether the primary process in the cadmium photosensitized reactions of these substances is

$$Cd(5^1P_1)+RH\rightarrow CdH+R$$

or

$$Cd(5^1P_1)+RH\rightarrow Cd(5^1S_0)+R+H.$$

[6] E. W. R. Steacie and D. J. LeRoy, J. Chem. Phys. **11**, 164 (1943).

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An Application of Probability Considerations to the Mechanism of the Photochemical Polymerization of Acetylene

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(Received April 9, 1943)

The series of experiments described in a recent paper led to an account of the mechanism of the photochemical polymerization of acetylene based upon the hypothesis that this process should be a chain reaction operating by cycles, each of them consisting of three stages, and that chain termination ought to depend upon the probability of formation of an aromatic nucleus among the polymers resulting from each particular cycle. While nothing is known of the intrinsic probabilities of the reactions postulated, the proposed mechanism seemed to offer an opportunity for quantitative treatment by the application of probability considerations. The present paper shows that if the probabilities of the formation of products of the addition and breaking of the easily dissociated single C−C bonds in the unstable products, in the respective stages of reaction, are assumed equal, quantum yields and heats of reaction may be calculated, which are in fair agreement with data found experimentally.

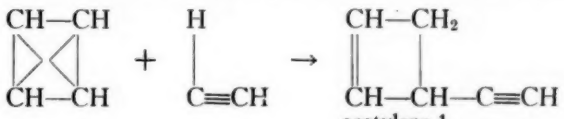
ACCORDING to evidence given in the previous paper,[1] in photoactivated acetylene in the gaseous phase there should occur polarization of the C≡C bond, and from both experimental and theoretical considerations it was concluded that the addition of a normal acetylene molecule to an activated one, following the previous association of these molecules, should give an activated cyclobutadiene molecule. No evidence was found suggesting the occurrence of any direct dimerization of acetylene molecules to vinylacetylene.

Similarly, the first stage of any other cycle of this reaction would consist of the association of a normal acetylene molecule to the activated C≡C bond regenerated in the growing polymer, followed by the formation of the activated cyclobutadiene ring.

Cyclobutadiene, or its derivatives, has not, so far, been obtained experimentally in any traceable amounts, this being usually attributed to the great strain to be expected, for stereochemical reasons, in the cyclobutadiene ring. But Wheland,[2] by use of the molecular orbital treatment, deduces that the cyclobutadiene ring in an activated state (i.e., lowest triplet state) ought to manifest properties analogous to those of the benzene ring in the ground state. This also justifies our expecting the reactions of activated cyclobutadiene to be similar to the reactions of benzene in the ground state. The addition, therefore, of an acetylene molecule to the activated cyclobutadiene molecule* should not cause any primary dissociation of the cyclobutadiene ring,** just as the benzene ring does not dissociate immediately in any reaction of the benzene molecule, but only as the result of some previous addition reaction to the ring. There would then exist two ways of acetylene reacting with a cyclobutadiene molecule:

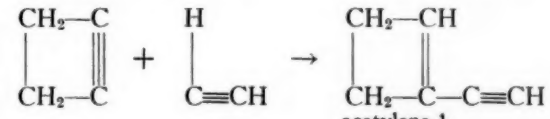
A: By association of acetylene by its C−H bond to cyclobutadiene:

1. Assuming for cyclobutadiene a structure like the Armstrong-Baeyer structure for benzene:



acetylene-1, cyclobutene-2.

2. Assuming the possible isomeric cyclobutine:



acetylene-1, cyclobutene-1.

[1] B. L. Dunicz, J. Am. Chem. Soc. **63**, 2461 (1941).
[2] Wheland, Proc. Roy. Soc. (London) **A164**, 397 (1938).

* In the subsequent discussion, since cyclobutadiene is always assumed to be formed in its activated state, no further description of its state will be made.

** Otherwise one would expect aliphatic trimers to be formed in the course of the reaction. But this is contrary to the experimental evidence.

B: By association of acetylene by its C≡C bond to cyclobutadiene:

1. Assuming for cyclobutadiene a structure like the Armstrong-Baeyer structure for benzene:

TABLE I. Likely and unlikely isomerizations of the unstable acetylene trimers *I*, *II*, *III*, involving breaking of a single C—C bond followed by intramolecular migration of not more than one hydrogen atom. The bond under consideration is dotted.

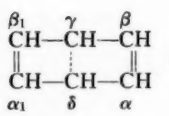
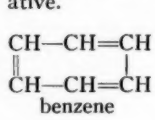
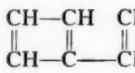
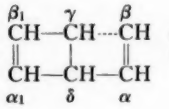
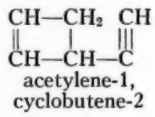
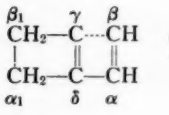
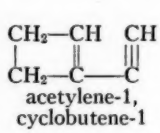
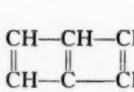
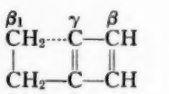
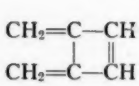
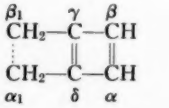
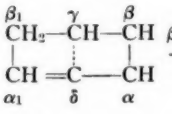
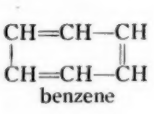
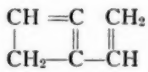
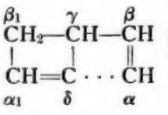
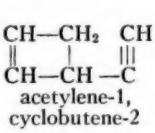
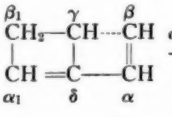
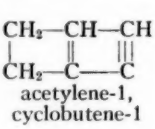
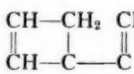
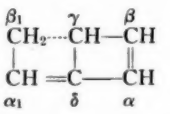
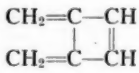
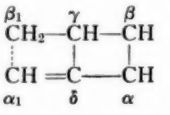
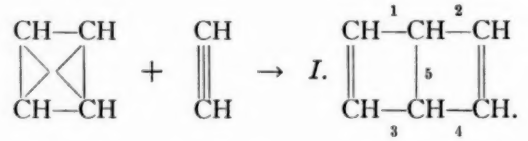
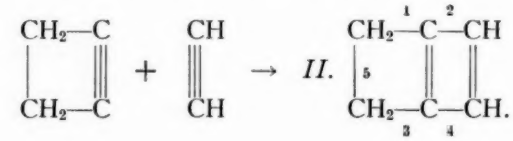
Unlikely products. Their structures should involve some further rearrangements into aliphatic compounds, that, however, have not been found experimentally.	H-atom migration	Unstable trimer of acetylene undergoing isomerization	H-atom migration	Likely products
		I with two stereochemically different types of C—C bond		All five single C—C bonds in *I* are likely to break giving in one case aromatic ring in other four the acetylene derivative.
			→	 benzene
	δβ ←		αγ →	 acetylene-1, cyclobutene-2
		II with three stereochemically different types of C—C bond		Only two single C—C bonds of the α, β, γ, δ, ring in *II* are likely to break giving the acetylene derivative.
			αγ →	 acetylene-1, cyclobutene-1
	α₁γ ←			
	←			

TABLE I.—*Continued*

Unlikely products. Their structures should involve some further rearrangements into aliphatic compounds, that, however, have not been found experimentally.	H-atom migration	Unstable trimer of acetylene undergoing isomerization	H-atom migration	Likely products
		III with five stereochemically different types of C—C bond		Only three single C—C bonds of the α, β, γ, δ, ring in *III* are likely to break giving in one case aromatic ring, in other two the acetylene derivative.
			β₁δ →	 benzene
	γα ←		βδ →	 acetylene-1, cyclobutene-2
			αγ →	 acetylene-1, cyclobutene-1
	α₁γ ←			
	γα₁ ←			

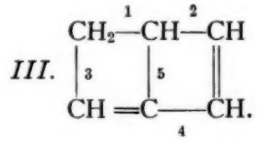


2. Assuming the possible isomeric cyclobutine:



3. The formation in either of the above reactions (*B*1 and 2) of the third trimer should also be possible:

III.



Owing to the undoubtedly unstable strained structure of the acetylene trimers *I*, *II*, *III*, it would be difficult to imagine that the process of adding acetylene molecules could continue beyond these products, without previous isomerization into some more stable forms occuring. In Table I are shown the isomerizations which might be involved. They are based on the assumption of only one single C−C bond breaking, this being followed by intramolecular migration of not more than one hydrogen atom. The products considered as likely would then be:

acetylene-1, cyclobutene-1,
acetylene-1, cyclobutene-2,
and benzene.†

In Table I the respective products of the isomerization reactions considered have been classified as likely and unlikely. Reactions are assumed to be likely when the breaking of a single C−C bond gives rise to an aromatic ring, or to an acetylene-cyclobutene structure with regeneration of an activated C≡C linkage capable of starting a new cycle of reactions by forming a cyclobutadiene ring with a new acetylene molecule. Reactions are considered unlikely if their products cannot be regarded as sufficiently strainless not to undergo further rearrangements to attain greater stability—such products never having been observed experimentally.

As the type *A* of reaction does not predict the possibility of benzene formation, in contradiction to the experimental findings of various investigators mentioned elsewhere,[1] one is tempted to conclude that the reaction which occurs is of the *B* type. This could also be deduced by considering that the triple bond is, because of its large accumulation of electrons, more liable than a homopolar, single, C−H bond, to polarization by induction. This makes possible the consequent association of acetylene, by its C≡C bond, to the cyclobutadiene molecule. If then we assume the *B* type of reaction as being the most likely, the simplest further assumption we can make is that the various fused-ring (bicyclic) structures which can be formed in this reaction, have equal chances of formation. Similarly in these fused-ring structures themselves, we assume equal chances for the breaking of the single C−C bonds capable of giving rise to those products of isomerization classified as "likely." The only satisfactory alternative to this would be to attempt to evaluate the intrinsic probabilities of the various reactions involved, by the kinetic treatment. But this, if possible at all, would be very complex.

With regard to the three unstable trimers: *I*, *II*, *III*, of acetylene, to be expected from the first cycle of reaction, there have been ascribed therefore equal chances for the dissociation of all five single C−C bonds, marked 1–5 with the probability $\frac{1}{5}$ for each, for the case of trimer *I*; equal chances for the dissociation of two bonds, marked 2 and 4, with the probability $\frac{1}{2}$ for each, making 1 for the whole system (as breaking either of these bonds would give the same result) for the case of trimer *II*; and equal chances for the dissociation of three bonds, marked 2, 4, and 5, with the probability $\frac{1}{3}$ for each, for the case of trimer *III*. Similar conditions have been assumed to apply to the successive cycles of the photochemical change of acetylene and also to the reactions of the mono- and di-substituted acetylenes, and on such considerations there have been worked out Tables III–VIII, containing totals of the probabilities (i.e., total yields) of the reactions occuring in particular cycles of the respective polymerizations. A better insight into Tables III–VIII is given by Table II, where is shown the probable effect of substituents on the breaking of the single C−C bonds in the unstable fused-ring structures produced in the second stages of the cycles. Breaking of the single C−C bond is considered improbable if the substituent replaces a hydrogen atom capable of migrating so as to complete isomerization into likely products, i.e., either a deactivated polymer

† This stands in agreement with experimental observations of the formation of benzene and naphthalene in the photochemical polymerization of acetylene pure and with added benzene, respectively, in the gaseous phase (see reference 1).

(containing an aromatic ring) or a polymer capable of further reaction by virtue of possessing an activated C≡C bond regenerated in it.

From the Tables III–VIII it was then possible to derive the following means of calculating quantum yields and heats of reaction for several acetylenes:

For the case of acetylene, one might illustrate schematically the whole course of its polymerization, as shown in Tables III–V, by depicting the course of the reaction assumed to take place in the first three of its cycles. In the formulae used in these tables the single, double, and triple intercarbon bonds are presented by means of single strokes, and double and triple strokes joined at the ends, respectively, carbon atoms being understood to be placed at their ends. The hexagon and the small bisected square denote

TABLE II. Effect of substituents on the breaking of the single C—C bonds in the unstable fused-ring structures produced in the second stages of the cycles. (The single C—C bonds capable of breaking are shown by dotted lines. Substituents which restrict bond breaking are represented by *R* and a number. Those unlikely to influence bond breaking are represented by *R**. Not more than one substituent is assumed to be possible on any carbon atom.

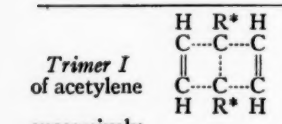
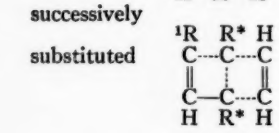
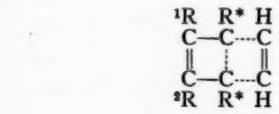
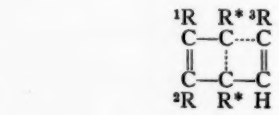
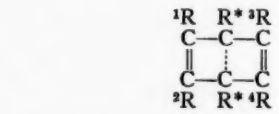
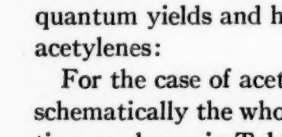
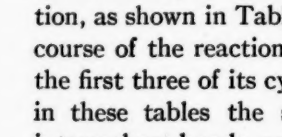
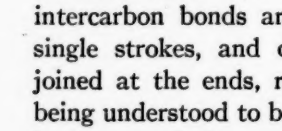
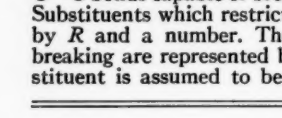
		Number of single C—C bonds capable of breaking to give likely products	Probability of formation of an aromatic nucleus	Probability of regeneration of an activated C≡C bond
Trimer I of acetylene successively substituted		5	1/5	4/5
		4	1/4	3/4
		3	1/3	2/3
		2	1/2	1/2
		1	1	0
Trimer II of acetylene successively substituted		2	0	1
		1	0	1
	 this if formed would probably decompose into original components	0	0	0
Trimer III of acetylene successively substituted		3	1/3	2/3
		2	1/2	1/2
		1	1	0

TABLE II.—*Continued*

benzene and cyclobutene rings, respectively. For simplicity the bonds between hydrogen and carbon atoms are not shown; their number and positions can be traced from the number of represented bonds meeting together, or from comparing the respective bond arrangements in these formulae with the formulae in Table II. In the interstices A_0, A_1, A_2, there are shown the first stages of reaction in the respective cycles: formation of an activated cyclobutadiene ring from two C≡C linkages, one of them being in an activated state. In the interstices B_0, B_1, B_2, there are shown all the possibilities, allowed by the postulated mechanism of reaction, for the formation of

the unstable products of the reaction between cyclobutadiene and the next acetylene molecule. These possible structures are derived by considering the combination of the substituents with the bonds in the cyclobutadiene/cyclobutine/ ring, so as to give all possible structural isomers. Differences between the substituents are ignored, the only condition required being that the associated acetylene molecule has one link in the C≡C bond opened in the addition reaction. The yield (probability of formation) of any of such products is taken as the reciprocal of the number of all possible structural isomers, permitted by the mechanism. In the interstices C_0, C_1, C_2, there are two columns showing in what proportion the unstable products formed in the second cycle would undergo isomerization into two classes of stable products: (*a*) those deactivated through formation in them of an aromatic ring,* and (*b*) those undergoing further reactions

TABLE III. The first cycle of the photochemical polymerization of acetylene. *A_0—1st stage of the cycle:* formation of an activated cyclobutadiene ring, non-, dimethyl-, or tetramethyl-substituted, from two acetylene, methylacetylene, or dimethylacetylene molecules, one of them being activated, respectively. (In case of methylacetylene two dimethylcyclobutadienes are possible; a yield of 1/2 for each is assumed.) *B_0—2nd stage of the cycle:* bonding of acetylene, methylacetylene, or dimethylacetylene molecule to the respective activated cyclobutadiene ring, formed in the first stage. The postulated mechanism of reaction would allow for primary formation of stereochemically different, unstable, fused-ring structures: three in case of acetylene with assumed yield 1/3 for each; twelve in case of methylacetylene with assumed yield 1/12 for each; and one in case of dimethylacetylene. *C_0—3rd stage of the cycle:* the unstable fused-ring structures formed in the second stage undergo rearrangement into either an aromatic nucleus (first column) causing deactivation of the product, or an acetylene-cyclobutene structure (second column) with activated C≡C bond regenerated, giving start to the second cycle of reaction. The derivation of the respective probabilities of rearrangement, shown by fractional values, is to be found in the text. The general result for the whole cycle is that from three moles of acetylene, methyl-, or dimethyl-acetylene, respectively, one mole being activated, there is formed: in the yield a_0—the deactivated trimer, i.e., one containing an aromatic nucleus; in the yield b_0—the reactive trimer containing a regenerated activated C≡C bond, giving start to the second cycle of reaction.

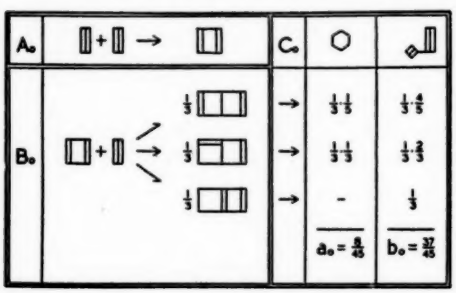
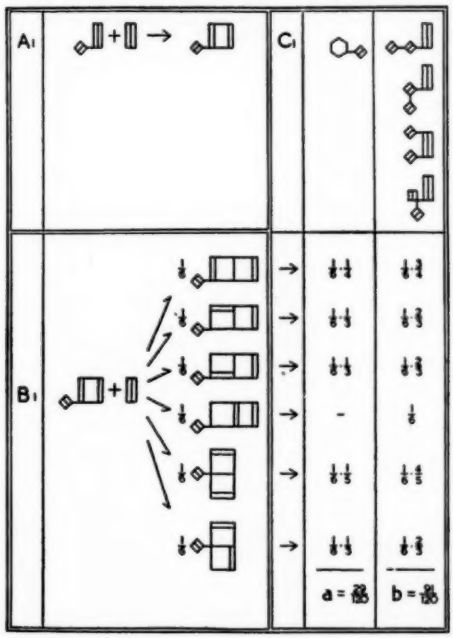
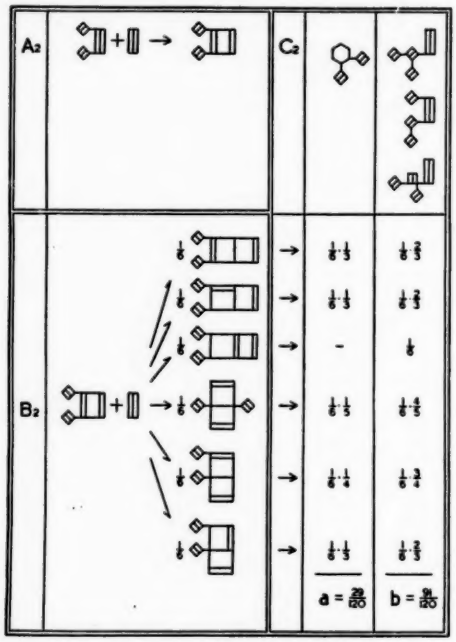


TABLE IV. The second cycle of the photochemical polymerization of acetylene. *A_1—1st stage of the cycle:* formation of an activated cyclobutadiene ring, mono-, or trisubstituted, through bonding of acetylene or methylacetylene molecule to the activated C≡C bond of the respective reactive trimer of acetylene or methylacetylene, resulting from the first cycle. *B_1—2nd stage of the cycle:* successive bonding of acetylene or methylacetylene molecule to the respective activated cyclobutadiene ring, formed in the first stage. The postulated mechanism of reaction would allow for primary formation, in each respective case, of six stereochemically different, unstable, fused-ring structures with yield 1/6 assumed for each (difference between methyl- and dimethylcyclobutenyl-substituents in case of methylacetylene reaction being neglected). *C_1—3rd stage of the cycle:* the unstable fused-ring structures formed in the second stage undergo rearrangement into either an aromatic nucleus (first column) causing deactivation of the product, or an acetylene-cyclobutene structure (second column) with activated C≡C bond regenerated, giving start to the third cycle of reaction. The derivation of the respective pobabilities of rearrangement, shown by fractional values, is to be found in the text. The general result for the whole cycle is that from one mole of reactive trimer (of acetylene or methylacetylene), resulting from the first cycle, together with two moles of acetylene or methylacetylene, there is formed: in the yield *a*—the deactivated pentamer, i.e., one containing an aromatic nucleus; in the yield *b*—the reactive pentamer containing a regenerated activated C≡C bond, giving start to the third cycle of reaction, in which the yields of the deactivated and reactive polymers will again be *a* and *b*, respectively.



* This is in accord with the observation that the concentration of benzene steadily increases during the reaction while that of other volatile products attains some stationary equilibrium concentration, whose value depends upon the kinetics of the reaction. If, on the other hand, deactivation of the growing polymer were not exclusively

TABLE V. The third cycle of the photochemical polymerization of acetylene. (The case of a reactive C≡C bond between two cyclobutene groups; the yields a and b of acetylene polymers, deactivated and undergoing the further reaction, respectively, should be the same as in case of cyclobutene groups at one end of the reactive C≡C bond.)

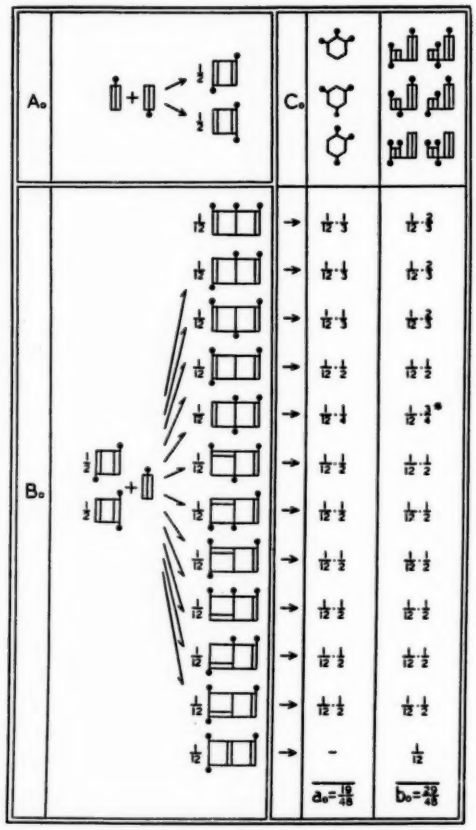


through regeneration in them of the activated C≡C linkage, these products being multiplied by the probability of formation of the unstable product of the second cycle. Their sums a_0 and b_0 or a and b, shown at the bottom of the tables, are the probabilities of formation in the cycle of the two respective classes of products.

In the case of methyl substituted acetylenes it is necessary to take into account the possibility that these compounds when activated, might undergo isomerization giving allenes, probably through intermediate formation of diradicals, e.g., $-CH_2-CH=CH-$, $-CH_2-CH=C(CH_3)-$. In the photochemical reactions of these compounds, therefore, twofold reactions might be expected to occur: (a) A reaction similar to that of acetylene, as shown in Tables VI–VIII (the symbolic formulae in these tables have the same significance as in previous tables with addition

associated with the formation of an aromatic nucleus (according to this derivation), one would expect to find also other volatile aromatic products, such as styrene or naphthalene, which, however, have not been experimentally observed.

TABLE VI. The first cycle of the photochemical polymerization of methylacetylene reacting in a similar way to acetylene. Some difference in further reacting of trimers with reactive C≡C bond having substituents at one and both ends may be neglected on account of the very small probability of the former).



of black circles (●) to represent methyl groups, and also in Table VII dimethylcyclobutenyl), with probabilities of formation of the two classes of products, deactivated and undergoing further reaction, different from those of the change of the acetylene, due to substituents. (b) Formation from the methylacetylene of an intermediate diradical, which then becomes deactivated by reacting with a second molecule of acetylene giving a hydroaromatic cyclopentadiene compound. This is shown in Table IX.

In the case of deuterium substituted acetylenes one would expect reduced mobility of the deuterium atom in the molecule as compared with the lighter hydrogen atom; monodeuteroacetylene should therefore show a yield intermediate between that for acetylene and that for methylacetylene undergoing type (a) reaction

(i.e., similar to that of acetylene), and dideuteroacetylene ought to show a still greater tendency to termination of reaction chains through the formation of aromatic rings.

Assume now the reaction to be started by one mole of activated acetylene molecules. As shown in Tables III, VI, and VIII, 3 moles of acetylene would be involved in the first cycle. Let a_0 be then the probability of formation of the aromatic nucleus from the three C≡C linkages of the respective acetylenes. It follows that the number of acetylene molecules used up in the formation of the deactivated polymer will be $3a_0$; at the same time the heat evolved by the formation of this product would be approximately $149a_0$ kcal. in this cycle.* In the formation of products capable of further reaction, the number of acetylene molecules used up would be $3b_0$ (where $b_0=1-a_0$); and the heat evolved will be approximately $88b_0$ kcal.** The $3b_0$ acetylene molecules used up in the formation of the reactive products, would combine in the second cycles, as shown in Tables IV and VII, with an additional $2b_0$ acetylene molecules. Hence for the polymer resulting from the second cycle the total number of acetylene molecules used up would be $(3+2)b_0$, of which $(3+2)b_0\times a$ would produce the new deactivated polymer (pentamer), the heat of reaction being approximately $(149+88)b_0\times a$ kcal.*** The number of moles of acetylene in the reactive products, resulting from the second cycle, will be $(3+2)b_0\times b$ (where $b=1-a$). These products would react further in the third cycle. It may be observed

TABLE VII. The second cycle of the photochemical polymerization of methylacetylene reacting in a similar way to acetylene. (Black circles denote methyl groups and also the dimethyl-cyclobutenyl groups which originated from the first cycle.)

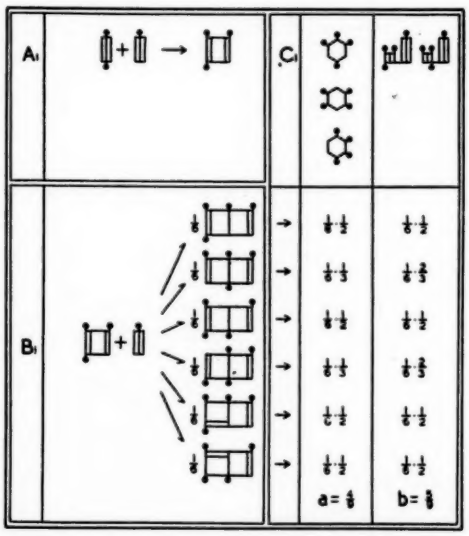


TABLE VIII. The photochemical polymerization of dimethylacetylene reacting in a similar way to acetylene. (From three moles—one activated—of dimethylacetylene molecules involved, all should yield hexamethylbenzene, this being deactivated.)

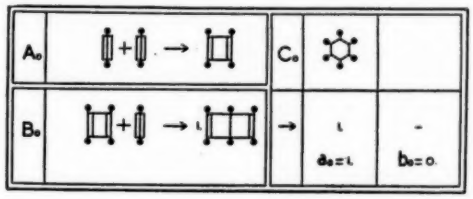
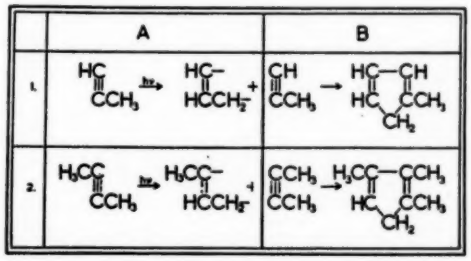


TABLE IX. The course of the photochemical polymerization of methyl- and dimethyl-acetylene, reacting through the formation of diradicals: $—CH_2—CH=CH—$, and $—CH_2—CH=C(CH_3)—$, respectively, upon activation. The products would be hydroaromatic dimers: methyl- and trimethyl-cyclopentadiene, respectively, these being deactivated.



* The heat of formation of the aromatic nucleus from three C≡C bonds is taken as the difference between the heat of combustion of three moles of acetylene ($3\times312.4=937.2$ kcal./mole) and one mole of benzene vapor (788 kcal./mole), i.e., 149.2 kcal. See Landolt-Börnstein, *Physikalisch-chemische Tabellen* (Berlin, 1923), series 5, Vol. 2, pp. 1588–9.

** Of the three C≡C bonds, with bond energy 123 kcal./mole each, reacting to form an acetylene-cyclobutene, two are being transformed into one C=C bond, with bond energy 100 kcal./mole, and four C—C bonds, with bond energy 58.6 kcal./mole each, the third C≡C being regenerated. Thus the heat of formation of the acetylene-cyclobutene system from acetylene would be the difference between the sum of bond energies of 1 C=C and 4 C—C bonds and the bond energies of 2 C≡C bonds, giving 88.4 kcal./mole of the product. See Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1942), second edition, pp. 53 and 131.

*** The product comprises the benzene-cyclobutene system formed from five C≡C bonds, three of them giving the benzene ring with evolution of 149 kcal./mole of benzene. The other two form the cyclobutene ring and the bond between benzene and cyclobutene rings, the heat of formation evolved being 88 kcal./mole.

TABLE X. Progress of formation of deactivated polymers in the photochemical polymerization of acetylene, started by a mole of activated acetylene molecules.

Number of cycle	Number of acetylene molecules in the polymer resulting from the cycle	Number of acetylene molecules producing a deactivated polymer in each cycle	Heat of reaction evolved in each cycle on formation of a deactivated polymer, in kcal./mole of activated acetylene molecules involved
1	3	$3a_0$	$149a_0$
2	5	$[3+2.1]b_0\times a$	$[149+88.1]b_0\times a$
3	7	$[3+2.2]b_0\times b\times a$	$[149+88.2]b_0\times b\times a$
4	9	$[3+2.3]b_0\times b^2\times a$	$[149+88.3]b_0\times b^2\times a$
–	–	– – – – – – – –	– – – – – – – – –
$n-1$	$3+2(n-2)$	$[3+2(n-2)]b_0\times b^{n-3}\times a$	$[149+88(n-2)]b_0\times b^{n-3}\times a$
n	$3+2(n-1)$	$[3+2(n-1)]b_0\times b^{n-2}\times a$	$[149+88(n-1)]b_0\times b^{n-2}\times a$

from the tables that each successive cycle would result in two additional acetylene molecules being brought into reaction in stoichiometric relation, as outlined in the Table X. Hence in the formation of the polymer resulting from the third cycle the total number of acetylene molecules involved would be $(3+2.2)b_0\times b$. The number of moles of acetylene in the deactivated polymer produced in the third cycle will be $(3+2.2)b_0\times b\times a$, and the evolved heat on its formation be approximately $(149+88.2)b_0\times b\times a$ kcal.†

For the cycles following the second one, the probability of formation of the deactivated polymer in each cycle would be always a (as in the second cycle), and the number of acetylene molecules forming a reactive polymer remaining after each cycle would be then b times the number of molecules contained in the reactive polymer resulting from the previous cycle, after the addition to it of 2 acetylene molecules in stoichiometric relation. Therefore, for the polymer resulting from the fourth cycle the number of moles used up would be $(3+2.3)b_0\times b^2$, and the number used up for the formation of the deactivated polymer would be $(3+2.3)b_0\times b^2\times a$, the heat evolved being $(149+88.3)b_0\times b^2\times a$ kcal. In the same way it may be shown that for the deactivated polymer of the nth cycle the number of molecules used up would be $(3+2(n-1))b_0\times b^{n-2}\times a$ and the heat evolved on its formation $(149+88(n-1))b_0\times b^{n-2}\times a$ kcal.

Hence the total number of acetylene moles involved in the polymerization initiated by one mole of activated acetylene molecules, with cycles running into infinity, would be:

$$\varphi=3a_0+\sum_{n=2}^{\infty}[3+2(n-1)]b_0\times b^{n-2}\times a$$

$$=3a_0+3a\times b_0\sum_{m=0}^{\infty}b^m+2a\times b_0\sum_{m=0}^{\infty}(m+1)b^m \quad \text{(putting } n-2=m\text{)}$$

$$=3a_0+3a\times b_0\times\frac{1}{1-b}+2a\times b_0\times\frac{1}{(1-b)^2} \quad \text{(by the binomial theorem)}$$

$$=3a_0+3b_0+\frac{2b_0}{a}$$

$$=3+2b_0/a.$$

This last quantity represents the theoretical quantum yield φ of the reaction.

Correspondingly, the heat evolved in the reaction would be:

$$149a_0+\sum_{n=2}^{\infty}[149+88(n-1)]b_0\times b^{n-2}\times a=149+88b_0/a \text{ kcal.}$$

To obtain the heat change per acetylene mole polymerized, this quantity must be divided by the quantum yield φ; thus the theoretical heat

† From the second cycle onwards the heat evolved in the formation of the deactivated polymer would be made up as follows:
(a) The heat of formation of the cyclobutene rings contained in it multiplied by the probability of formation of the polymer. The number of cyclobutene rings will be one less than the number of cycles, hence the heat evolved will be $88(n-1)$ kcal.
(b) The heat of formation of one aromatic nucleus terminating the chain of reaction, i.e., 149 kcal./mole. This is also multiplied by the probability of formation of the polymer.
The total heat of formation will be the sum of these two terms.

TABLE XI. Data for the photochemical and radiochemical polymerization of acetylene, methyl-, dimethyl-, deutero-, and dideutero-acetylene.

Compound	P calc.	P exp.	$M/2N$ exp.	Q kcal./mole of monomer calc.	Q kcal./mole of monomer exp.
CH≡CH	$P=9.8$	9.2±1.5 (6)	10–13 (5, 9, 10)	$Q\geqslant 45.7$	47 (10)*
CH_3—C≡CH	$2<P<5.7$	3.5 (7)	4.15 (2)	$47.1>Q>42.5$**	—
CH≡CD	$5.7<P<9.8$	—	—	$47.1>Q>45.7$	—
CH_3—C≡C—CH_3	$2<P<3$	—	2.9 (2)	$49.3>Q>42.5$**	—
CD≡CD	$3<P<5.7$	5 (3)	—	$49.3>Q>45.7$	—

* For radiochemical polymerization.
** Heat of formation of cyclopentadiene from acetylene and methylacetylene, on the basis of available data. See Landolt-Börnstein, *Physicalish-chemische Tabellen* (Berlin), series 5, Vol. 2, pp. 1588–9 (1923), and Vol. 3, p. 2896 (1936).

of reaction would be:

$$Q=(149+88b_0/a)/\varphi \text{ kcal.}$$

Since in the case of methyl and dimethyl acetylenes the chain of reaction might be stopped if these were to dimerize partially into methyl- and trimethyl-cyclopentadiene, respectively, the heat of polymerization of these compounds per mole acetylene polymerized should lie between the values calculated for their reaction in a similar way to acetylene, and one-half of the heat of formation of the cyclopentadiene ring from one C≡C and one C=C−C linkage, i.e., approximately 42.5 kcal./mole of acetylene polymerized.*

The final values of the quantum yield and heat of reaction for various acetylenes considered, as calculated by this method, are shown in Table XI, where they are compared with the available experimental data. In the case of the heats of reaction any additional heat which might be evolved in the secondary combination of unsaturated polymers could not be taken into account here, although this quantity might be appreciable and would make the heat of reaction more exothermic. As may be seen, there is good agreement between the experimental and the calculated values for all the compounds considered. The data suggest also that both the radiochemical and photochemical reactions follow a similar mechanism.

The somewhat larger yields in the radiochemical reactions of acetylenes under the influence of both alpha- and beta-rays[3–6] might possibly be due to the fact that ionization of acetylene molecules might be accompanied by polarization of some number of normal molecules. Moreover, because of the enormous energy released by the disintegration of radon,[7] one ought to expect a larger yield of aromatic products[6, 8–12] in the alpha-ray polymerization of acetylene than in the photochemical reaction, since it is well known that the effect on acetylene of a rise in temperature is to favor the formation of aromatic hydrocarbons. This should also provide an explanation for the observed temperature independence of the yield of the radiochemical reaction[4, 6] within the range 0°–100°C.

* The heat of formation of the cyclobutadiene ring has been taken as the difference between the sum of heats of combustion of acetylene and methylacetylene (312.4 kcal./mole of acetylene+473.6 kcal./mole of methylacetylene =786.0 kcal.) and the heat of combustion of liquid cyclopentadiene (701.0 kcal./mole, this being the only available value). See Landolt-Börnstein, *Physicalisch-chemische Tabellen* (Berlin), series 5, Vol. 2, pp. 1588–9 (1923), and Vol. 3, p. 2896 (1936).

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